

Docket No.: 05542/071002

(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:

Robert L. Horton et al.

Application No.: 10/620,041

Confirmation No.: 7482

Filed: July 15, 2003

Art Unit: 1712

For: SURFACTANT-POLYMER COMPOSITIONS

FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED

FLUID

Examiner: C. R. Richard

UNAVAILABILITY OF INVENTOR PETITION UNDER 37 C.F.R. § 1.47

MS AF Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

Dear Sir:

In response to the Petition Dismissal of January 11, 2006, please consider the following reply.

The Application lists seven inventors: Robert L. Horton, Bethicia B. Prasek, Frederick B. Growcock, David Kippie, John W. Vian, Kamila B. Abdur-Rahman, and Morris Arvie, Jr. A signed Declaration for Robert L. Horton, Bethicia B. Prasek, Frederick B. Growcock, David Kippie, John W. Vian, and Morris Arvie, Jr. in compliance with 37 C.F.R. § 1.68 was submitted with the filing of the application on July 15, 2003. Kamila B. Abdur-Rahman signed that Declaration but failed to date her signature. On November 14, 2005, a first Petition was filed, including chronological proof of the pertinent facts relating to the petitioners efforts to obtain the supplemental Declaration.

Subsequently, the first petition was dismissed for failure to submit a copy of the entire application, evidence of that transmittal submitted, proof of reasonable effort to ascertain a

current or last known address, and proof of due diligence effort ascertaining the same. Thus, in response to the dismissal, Petitioner submits a Declaration, made by Leah Bardin, which details attempts to contact Kamila B. Abdur-Rahman by additional means.

After a diligent effort, Leah Bardin has been unable to obtain a signed and dated supplemental Declaration from Kamila B. Abdur-Rahman. Leah Bardin has attempted to contact Kamila B. Abdur-Rahman via mail to her last known address, via mail to a second address on file with M-I L.L.C., via telephone book, internet, and telephone. Please find appended hereto an updated chronological proof of the pertinent facts relating to the petitioners efforts to obtain the supplemental Declaration:

Tab No.	Date(s)	Description
Tab 1	Assignment signed July 1, 2003	Assignment of rights to the invention known as "Surfactant-Polymer Compositions For Enhancing the Stability of Viscoelastic-Surfactant Based Fluid" to M-I L.L.C. by Kamila B. Abdur-Rahman
Tab 2	Declaration filed July 15, 2003	Signed Declaration of Robert L. Horton, Bethicia B. Prasek, Frederick B. Growcock, David Kippie, John W. Vian, and Morris Arvie, Jr. and undated Declaration of Kamila B. Abdur-Rahman accompanied the filing of the patent application titled "Surfactant-Polymer Compositiions For Enhancing the Stability of Viscoelastic-Surfactant Based Fluid," later designated by the U.S. Patent and Trademark Office as U.S. Patent Serial No. 10/620,041
Tab 3	Letter sent September 21, 2005	Certified letter containing application as filed and new Declaration sent to Kamila B. Abdur-Rahman at 12707 Bellaire Blvd. No. 303, Houston, Texas 77072. Certified letter returned to sender as "Attempted Not Known."
Tab 4	Letter sent April 21, 2006.	Certified letter containing application as filed and new Declaration sent to Kamila B. Abdur-Rahman at P.O. Box 1603, Alief, Texas 77411 Certified letter has not currently been received.
Tab 5	Declaration signed May 11, 2006	Declaration of Leah Bardin declaring first-hand knowledge of the pertinent facts

The last known residential address of Kamila B. Abdur-Rahman is:

12707 Bellaire Blvd. No. 303,

Houston, Texas 77072

A second known address for Kamila B. Abdur-Rahman is:

PO Box 1603

Alief, Texas 77411

In view of the petitioner's diligent attempts to obtain the signature of the unavailable inventor, enclosed documentation, and pursuant to 37 C.F.R. § 1.47(a), the petitioner requests that that the referenced application be examined without the signed Declaration of

A credit card form SB-08 for the petition fee is enclosed along with this Petition. Please apply any charges not covered, or any credits, to Deposit Account No. 50-0591, under Order No. 05542/071002 from which the undersigned is authorized to draw.

Dated: May 11, 2006

Kamila B. Abdur-Rahman.

Respectfully submitted,

ر V

effrey S Bergman

Registration No.: 45,925

OSHA LIANGLLP

1221 McKinney St., Suite 2800

Houston, Texas 77010

(713) 228-8600

(713) 228-8778 (Fax)

ASSIGNMENT

In consideration of the sum of one dollar (\$1.00) or equivalent and other good and valuable consideration paid to each of the undersigned: Robert L. Horton; Bethicia Prasek: Frederick B. Growcock; David Kippie; John W. Vian; Kamila B. Abdur-Rahman; Morris Arvie, Jr. the undersigned hereby sell(s) and assign(s) to M-I LLC. (the "Assignee"), a corporation of Delaware, having a place of business at 5950 North Course Drive, Houston, TX 77072, his/her entire right, title and interest

check applicable box(es) \(\sum \): for the United States of America (as defined in 35 U.S.C. \(\) 100), \(\sum \): and throughout the world,

in the invention(s) known as Surfactant-Polymer Compositions for Enhancing the Stailly Viscoelastic-Surfactant Based Fluid for which application(s) for Letters Patent in the United States of America has (have) been executed by the undersigned on evendate (also known as United States Patent Application No. 10/_______, filed_______, 2003), in any and all applications thereon, in any and all Letters Patent(s) therefor, and in any and all reissues, extensions, renewals, reexaminations of such applications or Letters Patent(s) and divisional and continuation applications thereof, to the full end of the term or terms for which such Letters Patent(s) issue, including all claims, if any, that may have arisen for infringement prior to the date of this assignment, such entire right, title and interest to be held and enjoyed by the above-named Assignee to the same extent as they would have been held and enjoyed by the undersigned had this assignment and sale not been made.

The undersigned agree(s) to execute all papers necessary in connection with the application(s) and any continuing (continuation, divisional, or continuation-in-part), reissue, reexamination or corresponding application(s) thereof and also to execute separate assignments in connection with such applications as the Assignee may deem necessary or expedient.

The undersigned agree(s) to execute all papers necessary in connection with any interference that may be declared concerning the application(s) or any continuing (continuation, divisional, or continuation-in-part), reissue or reexamination application thereof and to cooperate with the Assignee in every way possible in obtaining evidence and going forward with such interference.

The undersigned hereby authorizes and requests the government authority to issue any and all Letters Patent granted on such inventions to the Assignee.

The undersigned hereby warrants and represents that the undersigned has full right to convey the entire interest herein assigned, and that the undersigned has not executed, and will not execute, any agreement in conflict therewith.

The undersigned hereby expressly intends this agreement to be binding on the heirs, assigns, representatives and successors of the undersigned and extend to the successors, assigns and nominees of the Assignee.

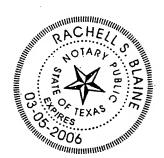
IN WITNESS WHEREOF, executed by the undersigned on the date(s) opposite their name(s).

Signature: Frederich B. Francol Date: 7-1-2003
Printed Name: Frederick B. Growcock
COUNTY OF HAVYIS STATE OF TEXAS) ss.
STATE OF $\underbrace{Te \times xa. }_{}$) ss.
BEFORE ME, the undersigned authority, on this / day of July 2003, personally appeared / Crowcolk, known to me to be the person whose name is subscribed to the foregoing instrument and acknowledged to me that he executed the same of his own free will for the purposes and consideration therein expressed.
Rowhell & Blains
[SEAL]
SAN PO STATE OF THE STATE OF TH
Signature: \ Date: 7/1/03
Printed Name: David Kippier
COUNTY OF Harris)
STATE OF Texas) ss.
BEFORE ME, the undersigned authority, on this 15th day of 1000, personally appeared 1000 kind kind kind known to me to be the person whose name is subscribed to the foregoing instrument and acknowledged to me that he executed the same of his own free will for the purposes and consideration therein expressed. Notary or Consular Officer
[SEAL]
RYCHILLIAN BOLD OF FETT SON OF THE SON OF TH

Signature: Date: Date: Date: 2003
COUNTY OF Harris
STATE OF $\frac{1-1\times as}{1}$) ss.
BEFORE ME, the undersigned authority, on this 2005, personally appeared John Vian, known to me to be the person whose name is subscribed to the foregoing instrument and acknowledged to me that he executed the same of his own free will for the purposes and consideration therein expressed.
Rochell & Blue
Notary or Consular Officer
[SEAL] Notary or Consular Officer ******
Signature: Kamila B. Abdur-Rahman Date: July 1, 2003
COUNTY OF Larris)
STATE OF $\frac{Te \times S}{S}$ ss.
BEFORE ME, the undersigned authority, on this 1st day of 2003, personally appeared Kantla Abdur - Rahman known to me to be the person whose name is subscribed to the foregoing instrument and acknowledged to me that he executed the same of his own free will for the purposes and consideration therein expressed.
Notary or Consular Officer
[SEAL]

Signature:
Printed Name: Morris Arvie, Jr.
COUNTY OF Harris) ss.
STATE OF TEXAS) ss.
BEFORE ME, the undersigned authority, on this day of, 20_0, personally appeared
Rochell & Blain
Notary or Consular Officer

[SEAL]



DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare as evidenced by my signature that:

My residential address, mailing address and citizenship are as stated below next to my name,

I believe that the below named inventor(s) are the original, first and joint inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SURFACTANT-POLYMER COMPOSITIONS FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED FLUID

the s	specification of which			
\boxtimes	is attached hereto.			
	was filed on			as
	Application Serial No.			
	and was amended			
		(if applicable)		 .
spec I ack appli	ification, including the clain nowledge the duty to disclo	ed and understand the conterns, as amended by any amense all information that may be itle 37, Code of Federal Regerates ***** NAL APPLICATION(S):	dment referred to be material to the	o above. e examination of this
provi claim provi discle occur	sional application(s) for pat as of this application is not of ded by the first paragraph of ose material information as	rity benefits under Title 35, ent listed below and, insofar lisclosed in the prior United f Title 35, United States Codefined in Title 37, Code of the prior provisional application:	as the subject m States application le, §112, I acknow Federal Regulation	natter of each of the on in the manner owledge the duty to ions, §1.56(a) which
60/3	19,575	September 25, 2002	copending	
(App	lication Serial No.)	(Filing Date)	(Status)	
I here	by appoint the following, e	**** ach associated with Custom	ier Number 275:	51, to prosecute this

-1-

application and to transact all business in the Patent and Trademark Office connected with this

application:

STEPHEN H. CAGLE, Attorney (Reg. No. 26,445), CARTER J. WHITE, Attorney (Reg. No. 41374), each an attorney or agent with the law firm of HOWREY SIMON ARNOLD & WHITE, LLP, and each associated with Customer Number 27551, as its attorney or agent so long as they remain with such law firm.

I direct that:

All correspondence be directed to:

Customer No. 27551 Place label here

HOWREY SIMON ARNOLD & WHITE, LLP
750 Bering Dr.
Houston, TX 77057

All telephone calls are to be directed to: Carter White, at telephone number: 713 268 1372.

I hereby declare, as evidenced by my signature below, that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

First Inventor's signature	RobertHarton	07/01/2 Date
First Inventor's Full Name		Dute
(Printed)	Robert L. HORTON	
Residential Address	1103 Springdale Ct.	
	Sugar Land, TX 77479	
	USA	
Mailing Address	Same as above	
Citizenship	US	

Second Inventor's signature (if any)	Beth B. Park	7-/-2013
(1. 11.)	Surpre 10. Village	Date
Second Inventor's Full Name	Rethicio	
	R-Bethica PRASEK	
Residential Address	2215 Avendia La Quinta, Apt 903	
	Houston, TX 77077	
	USA	
Mailing Address	Same as above	
Citizenship	US	

Third Inventor's signature	Frederick B. Growing	D . /
(if any)	- Mediral O. Drowcom	7-1-2003 Date
Third Inventor's Full Name		Date
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Residential Address	1514 Dodd Lane	
Residential Address	Houston, TX 77077	
	USA	
Mailing Address	Same as above	
Citizenship	US	
С		

		1,
Fourth Inventor's signature	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	7/1/22
(if any)	J. J. C. M.	Date
Fourth Inventor's Full Name		Date
(Printed)	David KIPPIE	
Residential Address	3610 Pedernales Trails Ln.	
	Katy, TX 77450	
	USA	
Mailing Address	Same as above	
Citizenship	US	

Fifth Inventor's signature (if any)	1.1.1	<u>y 200</u> 3
mini to a to that)	Y Date
Fifth Inventor's Full Name	T. I. MILYTANI	
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Residential Address	3317 Greenwood Pl.	
·	Deer Park, TX 77536	
	USA	
Mailing Address	Same as above	
Citizenship	US	

Sixth Inventor's signature (if any)	Kamla alda Kahna	
G: 4 7		Date
Sixth Inventor's Full Name	W. " D. ADDITO DATE (A)	
(Printed)	Kamila B. ABDUR-RAHMAN	
Residential Address	12707 Bellaire Blvd. # 303	
	Houston, TX 77072	
	USA	
Mailing Address	Same as above	
Citizenship	USA	

Seventh Inventor's signature (if any)	Moria amily 7/1/03	
		Date
Seventh Inventor's Full Name	·	
(Printed)	Morris ARVIE, Jr.	
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	USA	
Mailing Address	Same as above	
Citizenship	US	



5950 North Course · Houston, Texas 77072

Tel: 281.561.1300 · Fax: 281.561.1452 · www.miswaco.com

Writer's Direct Dial: 281.561.1451 Lbardin@miswaco.com

Via Certified Mail.

September 21, 2005

Ms. Kamila B. Abdur-Rahman 12707 Bellaire Blvd. #303 Houston, TX 77072

Re: U.S. Patent Application No. 10/620,041

Entitled: Surfactant-Polymer Compositions for Enhancing the Stability of Viscoelastic-

Surfactant Based Fluid

Inventors: Robert Horton, Bethicia B. Prasek, Frederick Growcock, David P. Kippie,

John Vian, Kamila Abdur-Rahman, Morris Arvie

M-I L.L.C. Ref: PA-00146US

Dear Ms. Abdur-Rahman:

We write you regarding the above-referenced U.S. application in which you are listed as an inventor. In July 2003, when the application was filed, you as well as the other inventors signed the Declaration. However, we have recently received a notice from the Patent Office that your signature is not dated, therefore they are requiring we submit a new declaration with a new signature and date.

We have enclosed a new Declaration for your execution as well as a copy of the application and original Declaration you signed. Please sign and date the new declaration and forward to us in the enclosed return FedEx envelope as soon as possible.

Please do not hesitate to contact me or Carter White at 281-561-1450 or cjwhite@miswaco.com should you have any questions. We appreciate your help with this matter.

Regards,

Leah S. Bardin Patent Paralegal

Encl.

cc: Carter J. White, Ph.D.

Item 4 if Restricted Delling's desired. Print your name and a continuous on the reverse so that we can return the part to you. Attach this card to the back of the mailpiece, or on the front if space permits. 1. Article Addressed to: 1. Article Addr	C. Signature X
#303 HOUSTON TX 77072	3. Service Type Certified Mail Registered Insured Mail C.O.D. 4. Restricted Delivery? (Extra Fee) Yes
2. Article Number (Copy from service label)	13400 00110 88795899

Domestic Return Receipt

Legal Dept. - Fatents
5950 North Course Drive
Houston, Texas 77072

MS. Kamila B. Abdur-Rahman
12707 Bellairé Blvd. #303
Houston, TX 77072

PS Form 3811, July 1999



102595-00-M-0952

I hereby certify that this correspondence is in an envelope addressed to: Commission	being deposited with the U.S. Postal Service as Express Mail, Airbill No. oner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on the date shown below.
Dated:	Signature:0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SURFACTANT-POLYMER COMPOSITIONS FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED FLUID

the specification of which was filed on July 15, 2003 as Application No. 10/620,041.

In the event that the filing date and/or Application No. are not entered above at the time I execute this document, and if such information is deemed necessary, I hereby authorize and request my attorneys/agent(s) at Osha · Liang LLP, 1221 McKinney St., Suite 2800, Houston, Texas 77010, to insert above the filing date and/or Application No. of said application.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment, if any, specifically referred to herein.

I acknowledge the duty to disclose all information known to me that is material to patentability in accordance with Title 37, Code of Federal Regulations, § 1.56.

FOREIGN PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

	of the application on which priority is claimed:
x no such foreign applications have been filed	o such foreign applications have been filed
such foreign application have been filed as follows:	uch foreign application have been filed as follows:

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Application Number	Country	Date of Filing	Priority Claimed Under 35 USC 119

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Country	Date of Filing
	Country

CLAIM FOR BENEFIT OF EARLIER U.S. PROVISIONAL APPLICATIONS

I hereby claim priority benefits under Title 3	5, United States Code §119(e), of any United
States provisional patent application(s) listed	below:

	no such U.S.	provisional	applications	have	been	filed
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Application Number	Date of Filing	Priority Claimed Under 35 USC 119
60/319,575	September 25, 2002	X Yes No

CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)

I hereby claim the benefit under Title 35, United States Code, §120 of the United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose all information that is material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56 which became available to me between the filing date of the prior application and the national or PCT international filing date of this application:

x no such U.S./PCT ap	plications have been	filed.	
such U.S./PCT applie	cation have been file	d as follows:	٠
Application Number	Relationship	Parent Application	Date of Filing

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Please mail all correspondence to Jeffrey S Bergman, whose address is:

Osha · Liang LLP 1221 McKinney St., Suite 2800 Houston, Texas 77010

Please direct telephone calls to: Jeffrey S. Bergman at (713) 228-8600.

Please direct facsimiles to: (713) 228-8778

Full name of sole or first inventor	
Robert L. Horton	
Sole or first inventor's signature	Date
Residence	
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Citizenship US	
Mailing Address	
1102 Contradata Ct	
1103 Springdale Ct. Sugar Land, Texas 77479	
Sugar Danes, Toxas 77477	
Full name of second inventor, if any	
Bethicia B. Prasek	
Second inventor's signature	Date
	·
Residence	
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Citizenship US	
Mailing Address	
2215 Assemble I - Outres And 202	
2215 Avenida La Quinta, Apt. 903 Houston, Texas 77077	
11000011, 10000 11011.	
Full name of third inventor, if any	
Frederick B. Growcock	
Third inventor's signature	Date
	·
Residence	
Houston, Texas	
Citizenship US	
Mailing Address	
1514 Dodd Lane	
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Troubled Total Trott	
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David P. Kippie	
Fourth inventor's signature	Date
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Mailing Address	
3610 Perdernales Trails Lane	
Katy, Texas 77450	

Full name of fifth inventor, if any	
John W. Vian	
Fifth inventor's signature	Date
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Mailing Address	· · · · · · · · · · · · · · · · · · ·
3317 Greenwood Pl.	
Deer Park, Texas 77536	
Full name of sixth inventor, if any	
Kamila B. Abdur-Rahman Sixth inventor's signature	
Sixui inventor's signature	Date
	a di
Residence	189tt /
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Citizenship US	
Mailing Address	
10000 D. H D	
12707 Bellaire Blvd. #303	
Houston, Texas 77072	•
Full name of seventh inventor, if any	
Morris Arvie	
Seventh inventor's signature	Date
Residence	
Houston, Texas	
Citizenship US	
Mailing Address	
Trading respices	
11655 Briar Forest #83	
Houston, Texas 77077	
	· · · · · · · · · · · · · · · · · · ·
Full name of eighth inventor, if any	
Fighth inventor's circustum	I Det
Eighth inventor's signature	Date
Residence	
Citizenship	
Mailing Address	

APPLICATION FOR UNITED STATES LETTERS PATENT

for

SURFACTANT-POLYMER COMPOSITIONS FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED FLUID

by

Robert L. Horton
Bethicia B. Prasek
Frederick B. Growcock
David Kippie
John W. Vian
Kamila B. Abdur-Rahman
and
Morris Arvie, Jr.

This application claims the benefit of U. S. Provisional Application No. 60/319,575, filed

September 25, 2002, the entire contents of which are incorporated by reference herein.

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BACKGROUND

When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. For the purposes of the present disclosure, such a fluid will be referred to as a "well fluid." Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (i.e., drilling into a targeted formation), transportation of cuttings to the surface, controlling formation pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which a well is being drilled, fracturing the formation in the vicinity of a well, displacing the fluid within a well with another fluid, cleaning a well, testing a well, emplacing spacer or fluid loss control pills at various points in the displacement, completion, or work-over process, emplacing a packer fluid in the completed wellbore during production, preparing the well for abandonment, abandoning the well or, otherwise treating the well or the formation. A commonly used type of well fluid is based on water-based solutions including brines. Brines, such as CaBr₂ brine, are commonly used as well fluids because of the ability to control the density of the solution over a wide density range. Further the brines are typically substantially free of suspended solids and brines typically do not damage the more common types of subterranean formations.

When drilling progresses to the level of penetrating a hydrocarbon-bearing formation, special care may be required to maintain the stability of the wellbore. Examples of formations in which problems often arise are highly permeable and/or poorly consolidated formation and thus a technique known as "under-reaming" may be employed. In conducting the under-reaming process, the wellbore is drilled to penetrate the hydrocarbon-bearing zone using conventional techniques. A casing generally is set in the wellbore to a point just above the hydrocarbon-bearing zone. The hydrocarbon-bearing zone then may be re-drilled to a wider diameter, for example, using an expandable under-reamer that increases the diameter of the wellbore. Under-reaming

usually is performed using special "clean" drilling fluids. Typically the "clean" drilling fluids used in under-reaming are aqueous, dense brines that are viscosified with a gelling and/or cross-linked polymer to aid in the removal of formation cuttings. The expense of such fluids limits their general use in the drilling process.

When the target subterranean formation has a high permeability a significant quantity of the drilling fluid may be lost into the formation. Once the drilling fluid is lost into the formation, it becomes difficult to remove. Removal of the aqueous based well fluids is desired to maximize the production of the hydrocarbon in the formation. It is well known in the art that calcium- and zinc-bromide brines can form highly stable, acid insoluble compounds when reacted with the formation rock itself or with substances contained within the formation. These reactions often may substantially reduce the permeability of the formation to any subsequent out-flow of the desired hydrocarbons. As should be well known in the art, it is widely and generally accepted that the most effective way to prevent such damage to the formation is to limit fluid loss into the formation. Thus, providing effective fluid loss control is highly desirable to prevent damaging the hydrocarbon-bearing formation. For example such damage may occur during, completion, drilling, drill-in, displacement, hydraulic fracturing, work-over, packer fluid emplacement or maintenance, well treating, or testing operations.

Techniques that have been developed to control fluid loss include the use of fluid loss control "pills." As the term is used in this disclosure a "pill" is a quantity of fluid added to the well fluid so as to temporarily change the properties of the well bore fluid at or near a specific point in the well bore. Significant research has been directed to determining suitable materials for the fluid loss pills, as well as controlling and improving the properties of the fluid loss pills. Typically, fluid loss pills work by enhancing filter-cake buildup on the face of the formation to inhibit fluid flow into the formation from the wellbore; however the fluids in accordance with the claimed subject matter are effective by developing extremely high viscosity in the environment at and just within the face of the formation to inhibit fluid flow into the formation from the wellbore. Because of the high temperatures, high shear (caused by the pumping and placement of the pill), high pressures, and low pH to which well fluids may be exposed (i.e., "stress

conditions"), synthetic polymeric materials typically used to form fluid loss pills and to viscosify the well fluids tend to degrade rather quickly.

One class of viscosifiers commonly used in the petroleum industry comprises polymeric structures starting with molecular weights of hundreds of thousands to several million grams per mole. These large, chemically bonded structures are often crosslinked to further increase molecular weight and effective viscosity per gram of polymer added to the fluid. These large molecules are quite stable under the thermal conditions typically encountered in a subterranean reservoir. However, this thermal stability is believed to contribute to decreased well productivity. As a result, expensive and often corrosive breakers have been designed to destroy the molecular backbone of these polymeric structures. These breakers are typically oxidizers or enzymes and are at best only partially effective with typical reservoir cleanup less than 80% complete and more usually much less than 50% complete. It is also reported in the literature that the long term stability of polymeric based thickening agents is shortened by the high temperature, high shear, high pressures, and low pH to which well fluids may be exposed (i.e., "stress conditions").

Viscoelastic surfactants are commonly used in the petroleum industry as an alternative to the above mentioned polymeric thickening agents. Viscoelastic surfactants are relatively small molecules with each molecule being typically less than 500 grams per mole (i.e., molecular weight less than 500). These small molecules will associate under certain conditions to form structures which resemble the polymer molecules but which are not stable structures. The individual molecules of surfactant begin to associate to form rod-like or spiraling-cylinder-like micelles. These micelle structures are always in an equilibrium state of breaking and reforming. As dynamic structures, these polymer-shaped micelles are readily destroyed by shear, presence of hydrocarbons or increased temperature. While these features are desirable especially in a hydrocarbon-bearing formation, there is minimal control over the conditions under which micelle breakup occurs. Therefore, under conditions of exposure to oil, high temperature, high shear, or other "stress conditions", the viscoelastic surfactants rapidly return to their original small independent spherical micellar state. When the viscoelastic micelles are broken down to

this small independent spherical micellar state, the desired viscous nature of the well fluid is lost. In some cases the loss is temporary, in others the loss may be more permanent.

Presently there exists an unmet need for a simple, inexpensive way to increase the thermal range for viscoelastic-surfactant-based viscosifying agents used in downhole applications. Preferably, this thermal extender would be applicable to various viscoelastic-surfactant-based viscosifying agents.

SUMMARY

Upon review of the following disclosed and claimed subject matter, one of skill in the art should appreciate and understand that one illustrative embodiment is a wellbore fluid that includes: an aqueous based continuous phase; a viscoelastic surfactant; and a surfactant-polymer compound soluble in an aqueous solution. The surfactant-polymer compound has a molecular structure including a hydrophobic backbone and a plurality of hydrophilic functional groups attached to the hydrophobic backbone. The hydrophobic backbone is the reaction product of one or more molecules having polymerizable alkene or alkyne functional groups, for example an oligo- or poly-ethylene structure. In contrast the hydrophilic functional groups can be zwitterionic surfactant functional groups, anionic surfactant functional groups, cationic surfactant functional groups, and nonionic surfactant functional groups. The illustrative embodiment is molecularly designed such that the combination of the viscoelastic surfactant and surfactant-polymer compound forms micellar assemblies in the wellbore fluid. In one illustrative and exemplary embodiment the acid form of the surfactant-polymer compound has the structure:

in which x has a value of 2 to 300,000 and preferably x has a value of 2 to 36 Alternatively, the surfactant-polymer compound can be a salt of oligo- or poly-(α -alkenyl - ω - or α -alkynyl - ω -quaternary-ammonio-N-N-dialkyl-N-alkylcarboxylate) or a mixture further comprising a salt of N-alkyl-N-carboxymethyl-N,N-dimethylammonium chloride. Another alternative and illustrative embodiment is where the surfactant-polymer compound is a salt of oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate) or a mixture further comprising a salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride. A third alternative is where the surfactant-polymer compound is a salt of oligo- or poly-(α -alkenyl - α - or α -alkynyl - α -quaternary-ammonio-N,N-dialkyl-N-alkylcarboxylate), or is a salt of oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate).

 Additional embodiments of the claimed subject matter include zwitterionic surfactant heads such that the polymers or oligomers have the following structures:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

$$R_8$$
 is
$$\begin{bmatrix} CH_2 \\ CH_2 \end{bmatrix}_u$$

$$R_9$$
 is
$$\begin{array}{c|c} R_{11} \\ \hline CH_2 \\ \hline \\ R_{12} \end{array}$$

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3, and x + y + z = 3 to 300,000 and $S_1 = CO_2$ or SO_3 . In a preferred illustrative embodiment, t = 12 to 16, $\mu = 6$ to 12; v = 12 to 18, w = 1 to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

Alternatively the oligomer or polymer compound can be cationic in the surfactant head and thus have a structure such as:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

25
26
$$R_7$$
 is
$$CH_2 - CH - CH - R_{10}$$
27
OH OH

R₈ is
$$CH_2$$
 CH_3

R₉ is CH_2 R_{11}

R₉ is CH_2 R_{12}

R₁₁

R₁₂

R₁₂

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000. An especially preferred and illustrative embodiment includes an oligomer or polymer in which t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

In yet another illustrative embodiment, the oligomer or polymer can have a molecular structure that includes an anionic surfactant functional group such as:

where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

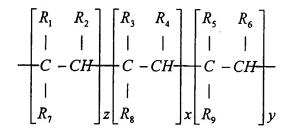
$$\begin{array}{ccc}
24 & & & \\
25 & & R_8 \text{ is} & & & \\
26 & & & & \\
\end{array}$$

28
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$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{11}
 R_{12}

1 2

in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to 300,000, and $S_1 = CO_2$ or SO_3 . In one such illustrative embodiment, it is preferred that t = 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

Further as noted above, the illustrative oligomer or polymer can have a nonionic surfactant group and preferably has a molecular structure such as:



in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_7$$
 is

 CH_2
 CH
 CH
 CH
 CH
 CH
 CH

17
18
$$R_8$$
 is
$$\begin{bmatrix} CH_2 \\ u \end{bmatrix}$$

$$R_9$$
 is
$$CH_2 \longrightarrow N - CH_2 - S_1$$

$$R_{12}$$

and in which, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000. In such instances, a preferred illustrative embodiment is

achieved when t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

Fundamentally the polymeric backbone can be saturated as noted in the above illustrative examples or unsaturated. In such illustrative embodiments, the oligomer or polymer has a back bone structure such as the following:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3 . As for the R_7 , R_8 and R_9 groups, these may

be the same as those disclosed above. Thus one of skill in the art should appreciate that zwitterionic, cationic, anionic and nonionic surfactant groups may be attached to the unsaturated backbone structure shown above and that such compounds are illustrative of

the disclosed and claimed subject matter.

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As discussed above, the novel oligomers and polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic surfactant systems. The conventional viscoelastic-surfactant-based fluids useful for the claimed subject matter are those in the following references, all of which are incorporated herein by reference - Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557. 6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168, Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322. Of these, the preferred viscoelastic-surfactant-based fluids are those based on anionic, cationic, or zwitterionic surfactants or mixtures of anionic and nonionic surfactants or mixtures of cationic and nonionic surfactants or mixtures of zwitterionic and nonionic surfactants. And of these, the particularly preferred viscoelastic-surfactant-based fluids

are those based on zwitterionic surfactants or mixtures of zwitterionic and nonionic surfactants. In both the preferred viscoelastic-surfactant-based fluids, and in the particularly preferred viscoelastic-surfactant-based fluids, a minority amount of an additional surfactant, termed a "co-surfactant", such as, for example, 2-ethylhexanol or SDBS may optionally be employed. The viscoelastic oligomers or polymers of the claimed subject matter may be created in the presence of conventional viscoelastic surfactant systems or may be synthesized in separate steps, optionally processed or dried, and then subsequently admixed into a solution of conventional viscoelastic surfactants.

It has been found that the oligomers or polymers of the illustrative drilling fluids can be crosslinked with polyvalent metal ions, formaldehyde, or glutaraldehyde. In one such embodiment, the polyvalent metal ions are selected from: Fe²⁺, Cd²⁺, Co²⁺, Ca²⁺, Cu²⁺, UO₂²⁺, PbO²⁺, Al³⁺, Fe³⁺, Cr³⁺, Ce³⁺, Ti⁴⁺, Zr⁴⁺, Sn⁴⁺ and mixtures thereof.

One of skill in the art should also appreciate that the disclosed and claimed subject matter includes a method of making a wellbore fluid as is disclosed herein. In one such illustrative embodiment, the method involves the blending of an aqueous fluid phase, a viscoelastic surfactant, a water-soluble inorganic salt, and an oligomer or polymer soluble in the aqueous salt solution. The oligomer or polymer includes a hydrophobic oligomeric or polymeric backbone made from the oligomerization or polymerization of alkene or alkyne monomer groups, or mixtures thereof. The oligomer or polymer further comprises surfactant functional groups attached to the hydrophobic backbone, wherein the oligomer or polymer is hydrophilic in the surfactant functional groups and hydrophobic in the backbone hydrocarbon chain. Thus the oligomer or polymer has a molecular structure that promotes the formation of micellar assemblies such that the oligomers or polymers develop viscoelastic character prior to a polymerization step.

The claimed subject matter also encompasses a method of drilling a subterranean well as well as other sues for the wellbore fluid that should be apparent to one of skill in the art.

Further details regarding the claimed subject matter can be found in the following description.

DESCRIPTION

The claimed subject matter relates to compositions for increasing the thermal durability of viscoelastic-surfactant-based well fluids. More specifically, the claimed subject matter relates to the fields of fluid rheology, thickeners, viscosifiers, viscoelastic fluids, viscoelastic surfactant fluids, drilling fluids, well fracturing fluids, well treatment fluids and fluid control pills. Further, the claimed subject matter relates to increasing the thermal and pressure stability of well fluids viscosified using viscoelastic surfactants by including an effective amount of a surfactant-oligomeric or surfactant-polymeric compound that has a thermally stable backbone structure and viscoelastic surfactant appendages. As the term is used in the present disclosure, "effective" simply means an amount sufficient to raise the temperature stability of the viscoelastic-surfactant based well fluid system by a measurable amount.

In accordance with one illustrative embodiment of the claimed subject matter, a sufficient quantity of at least one surfactant-oligomeric or surfactant-polymeric compound that is soluble in an aqueous salt solution is employed to affect the desired viscosity. In the claimed subject matter, the molecules of the surfactant-oligomeric or surfactant-polymeric compound have a hydrophobic oligomeric or polymeric backbone made preferably from the oligomerization or polymerization of alkene and/or alkyne groups. As the term is used herein, "thickener" and surfactant-oligomeric or surfactantpolymeric compound are used interchangeably and are intended to mean the compounds substantially described and claimed herein. The thickener of the claimed subject matter also includes chemical functional groups that are structurally similar to prior art viscoelastic surfactants and therefore these molecules exhibit similar chemical characteristics of prior art viscoelastic surfactants. Thus the hydrophobic backbone is chemically linked to and thus rendered at least in part hydrophilic by the presence of these chemical functional groups. One such illustrative compound is the product of the oligomerization reaction of a monomer such as the sodium salt of N-N-dimethyl-Nmethylcarboxylate-N-1-hepten-7-ammonium chloride to give the sodium salt of oligo-(1hepten-7-quaternary-ammonio-N-N-dimethyl-N-methylcarboxylate). oligomer is believed to have the simplified structure as indicated below in the acid form rather than the sodium-salt form:

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in which x will have a value from about 2 to several hundred thousand, preferably from about 2 to several dozen. The monomer may be prepared, for example, by the reaction of N-hexadecyl-N,N-dimethylamine with chloroacetic acid to produce N-hexadecyl-N-methylcarboxylic acid-N,N-dimethylammonium chloride. Upon neutralization with sodium hydroxide, the final product is the zwitterionic betaine which is the sodium salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride – it has a negative charge on the carboxyl group and the sodium cation associated with it as a counter ion, and a positive charge on the quaternary amine group and the chloride anion associated with it as a counter ion. Alternatively, the sodium and chloride counter ions may be separated therefrom, leaving the negatively charged carboxyl group and the positively charged quaternary amine group as counter ions for each other.

The sodium salt of oligo-(1-hepten-7-quaternary-ammonio-N-N-dimethyl-N-methylcarboxylate) is an example of a salt of oligo- or poly-(α -alkenyl- ω -quaternary-ammonio-N-N-dialkyl-N-alkylcarboxylate). This example begins to define the terms α -alkenyl- ω - and α -alkynyl- ω -, wherein the " α -" designation denotes a location at or near one end of the hydrocarbyl chain, such as, for example at the 1-, 2-, or 3- position and wherein the " ω -"designation denotes a location at or near the opposite end of the hydrocarbyl chain from the α -position, such as, for example at the very end of the hydrocarbyl chain, at one carbon group away from the very end of the hydrocarbyl chain,

or at two carbon groups away from the very end of the hydrocarbyl chain. An α -alkene and an α -alkyne are defined similarly. An α -alkenyl— ω -carboxylate salt and an α -alkynyl— ω -carboxylate salt are defined in a parallel manner. An α -alkenyl— ω -N,N,N-trialkylammonium salt are defined similarly. An α , α +2-alkadienyl— ω -carboxylate salt and an α , α +2-alkadiynyl— ω -carboxylate salt are defined in a parallel manner.

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In one illustrative embodiment, a monomer like the sodium salt of Ncarboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride could be mixed into the solution of the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles of the viscoelastic surfactant that is the sodium salt of N-hexadecyl-Ncarboxymethyl-N,N-dimethylammonium chloride. This illustrative monomer, the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride. differs only in minor ways from the sodium salt of N-hexadecyl-N-carboxymethyl-N.Ndimethylammonium chloride. Accordingly, the monomer will be readily subsumed into the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon one can take well-known steps to initiate the oligomerization or polymerization of the monomer to produce the sodium salt of oligo- or poly-(1-hepten-7quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate). This oligomer or polymer will be inherently hydrophilic in its zwitterionic functional groups and hydrophobic in the hydrocarbon chains that link all the zwitterionic functional groups to each other. The oligomer or polymer is believed to be structurally quite similar to the viscoelastic surfactant molecules in the well fluid and therefore is soluble or dispersible in the well fluid solution. Similar oligomers or polymers are likewise soluble or dispersible in other viscoelastic surfactant solutions such as 10% XE862 (a product that is commercially available from Schlumberger) solution with 0.3% sodium dodecylbenzene sulfonate (SDBS) in 13.5 pound per barrel CaBr₂-based brine. Upon mixing the oligomer or polymer with the viscoelastic-surfactant-based fluid, the oligomer or polymer is believed to be subsumed into the rod-shaped or spaghetti-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiraling-cylinder-like micelles is one or more such oligomer or polymer molecules and when configured in this fashion, the oligomer or polymer molecules impart greater thermal stability to the micelles, greater resistance to

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shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to oil, high shear in pumping and placement, high temperature, high differential pressure, and low pH.

Another illustrative embodiment of the compounds of the claimed subject matter includes the oligomeric or polymeric products of the co-oligomerization or co-polymerization of two different monomers such as 1-heptene and the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride. Alternatively, 1-heptene can be first co-oligomerized or co-polymerized with N,N-dimethyl-1-hepten-7-amine and in a subsequent reaction the amine groups are reacted with 1-chloro-propane-3-sulfonic acid and then caustic to produce oligo- or poly-(1-heptene-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). The resulting oligomer or polymer is believed to have the simplified structure as indicated below:

$$\begin{array}{c|c} \hline CH-CH_2 \\ \hline CH_2 \\$$

in which x and y will have values dependent upon the molar ratio of reactants added to the polymerization reaction and the sum of x and y will have a value of about 2 to several hundred thousand, preferably from about 2 to several dozen. While this oligomer or polymer will be inherently hydrophilic in its zwitterionic functional groups, there are two sources of hydrophobicity: in the 1-heptene co-oligomer or co-polymer species and in the hydrocarbon chains that link all the zwitterionic functional groups to each other. By

varying the molar ratio of the monomers present during the oligomerization or polymerization reaction, the hydrophobicity and viscoelastic surfactant properties of the resulting oligomer or polymer may be controlled. The oligomer or polymer contains a point of structural similarity to the small molecule viscoelastic surfactants and therefore is soluble or dispersible in such conventional viscoelastic surfactant solutions. Similar oligomers or polymers are likewise soluble or dispersible in the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr2-based brine discussed above. Upon admixing the polymer with the viscoelastic-surfactant-based fluid, the polymer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling—cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiraling—cylinder-like micelles is one or more such polymer molecules and when configured in this fashion, the polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill—including, for example, exposure to oil, high shear in pumping and placement, high differential pressure, and low pH.

Yet a third illustrative embodiment of the compounds of the claimed subject matter includes the co-oligomerization or co-polymerization of three or more co-monomers. For example, one could co-oligomerize or co-polymerize 1-heptene, 1-heptene-6,7-diol and N,N-dimethyl-1-hepten-7-amine. In such an illustrative embodiment, the amine groups are reacted with 1-chloro-propane-3-sulfonic acid and then caustic to produce oligo- or poly- (1-heptene -co-1-heptene-6,7-diol -co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). The resulting oligomer or polymer is believed to have the simplified structure as indicated below:

in which x, y and z will have values dependent upon the molar ratio of reactants added to the polymerization reaction and the sum of x, y, and z will have a value of about 3 to several hundred thousand, preferably from about 3 to several dozen. As with the other oligomers or polymers of the claimed subject matter, the above illustrative oligomer or polymer is soluble or dispersible in conventional viscoelastic surfactant well fluids such as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr2-based brine discussed above. Upon admixing the illustrative oligomer or polymer with such a viscoelastic-surfactant-based fluid, the oligomer or polymer is believed to be subsumed into the rod-shaped spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped spaghetti-like or spiraling-cylinder-like micelles is one or more such oligomer or polymer molecules and when configured in this fashion, the oligomer or polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill - including, for example, exposure to oil, high shear in pumping and placement, high differential pressure, and low pH. Additionally, the co-monomer 1-heptene-6,7-diol incorporates a vicinal diol functionality into the oligomer or polymer. Surface forces should cause the

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vicinal diol functionality to present itself at the outer surface of any rod-shaped micelle in which it has become subsumed.

The vicinal diol functionality provides the chemical functional group that renders the oligomers or polymers readily crosslinkable with polyvalent metal ions or complexes such as, for example, a borate, titanate, or zirconate crosslinker as taught in U. S. Patent 5,062,969, (2) divalent, trivalent, or tetravalent cations such as, for example, Fe²⁺, Cd²⁺, Co^{2+} , Ca^{2+} , Cu^{2+} , UO_2^{2+} , PbO^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Ce^{3+} , Ti^{4+} , Zr^{4+} , Sn^{4+} , and the like, (3) complexes of or other moieties containing the crosslinkers listed above in the first two categories, such as, for example, the tetrammine complex of the Cu2+ cation, the carbonate anion complexes of the UO₂²⁺ cation, UO₂(CO₃)₂²⁻ and UO₂(CO₃)₃⁴⁻, or the triethanolamine complex of the Ti⁴⁺ cation, (4) so-called "organic crosslinkers" such as, for example, formaldehyde, and glutaraldehyde, and (5) mixtures of the crosslinkers listed above in the first four categories and/or reaction products therefrom. Thus it is contemplated that one of skill in the art could, if desired, crosslink the illustrative oligomers or polymers with polyvalent metal ions, complexes, organic crosslinkers, or mixtures thereof, as described above. This is believed to lead effectively to the crosslinking of the viscoelastic surfactant assemblies in which the oligomers or polymers have been subsumed.

One of skill in the art should at this point appreciate that the co-oligomerization or co-polymerization reactions disclosed above result in the random placement of each co-monomer along the vinyl backbone of the illustrative oligomers or polymers. However, it is contemplated that block co-oligomerization or co-polymerization could also be used to achieve substantially similar results. Alternatively, block co-oligomerization or co-polymerization could also be used to carefully tailor the properties of the resulting oligomers or polymers made in accordance with the claimed subject matter. One of skill in the art should understand and appreciate that by systematically controlling the molar ratio of and concentration of monomers present in during the oligomerization or polymerization process, the order of addition, the temperature and duration of oligomerization or polymerzation and the initiators and catalysts used and their concentrations, the properties of the compounds of the claimed subject matter can be carefully controlled and tailored.

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Other oligomers or polymers formulated in accordance with and illustrative of the claimed subject matter include such oligomers or polymers as oligo- or poly-(N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-(N,N-diallyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-(1-butene-co-N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly- (1-butene-co-1-pentene-4,5-diol- co-N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-alkenyl or -alkynyl DMAPA amides (see Figure below), oligo- or poly-alkenyl or -alkynyl DMAPA quats, and oligo- or poly-alkenyl or -alkynyl tallow amine quaternary amines such as

C₁₂₋₂₂ DMAPA Amide

C₁₂₋₂₂ DMAPA Amide Quaternary Amine

Tallow Amine Quaternary Amine

$$R \longrightarrow N \subset I$$

and the like.

Except for the oligo- or poly-alkenyl or -alkynyl DMAPA amides, oligo- or poly-alkenyl or -alkynyl DMAPA quaternary amines, and oligo- or poly-alkenyl or -alkynyl tallow amine quaternary amines, oligomers or polymers of this type may be unlike those of the previous illustrative embodiments of the claimed subject matter in that they are probably not capable of effectively vacuuming up the micelles and packing them about themselves until there are enough surfactant molecules present in the vicinity of the oligomer or polymer molecule so that the spherical micelles can merge into a single rod-shaped or spaghetti-like or spiraling—cylinder-like micelles with the oligomer or polymer molecule subsumed within the rod-shaped or spaghetti-like or spiraling—cylinder-like micelles. Polymers or oligomers in accordance with the present illustrative embodiment

of the claimed subject matter are designed to be compatible with CaBr₂-, CaBr₂/CaCl₂-, ZnBr₂/CaBr₂-, and ZnBr₂/CaBr₂-/CaCl₂-based brines.

Other oligomers or polymers formulated in accordance with and illustrative of the claimed subject matter include oligomers or polymers such as oligo- or poly-(ethyleneco-N,N-diallyl-N,N-dimethyl ammonium chloride), oligo- or poly-(1-butene-co-N,Ndiallyl-N.N-dimethyl ammonium chloride), oligo- or poly-(1-butene-co-1-pentene-4,5diol-co-N.N-diallyl-N.N-dimethyl ammonium chloride), and the like. oligomers of this type are probably not sufficiently compatible with CaBr₂-, CaBr₂/CaCl₂-, ZnBr₂/CaBr₂-, and ZnBr₂/CaBr₂/CaCl₂-based brines; however, they expand the scope of the claimed subject matter into useful dimensions to the extent that these polymers should be quite compatible with NaCl-, NaBr-, NaBr/NaCl-, CsBr/KBr-, and CsBr/KBr/NaCl-based brines and the like. Poly-or oligo-(1-butene-co-1-pentene-4,5-diol-co-N,N-diallyl-N,N-dimethyl ammonium chloride) incorporates a vicinal diol functionality, and so one of skill in the art should appreciate that this polymer or oligomer may be crosslinkable with polyvalent metal ions as disclosed above. As noted above, when the oligomers or polymers are crosslinked with polyvalent metal ions, we also effectively crosslink the viscoelastic surfactant assemblies in which the oligomers or polymers have been subsumed.

Additional embodiments of the claimed subject matter include zwitterionic surfactant heads such that the polymers or oligomers have the following structures:

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in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_7$$
 is
 CH_2
 CH
 CH
 CH
 CH
 OH
 OH

$$R_8$$
 is CH_2 CH_2 CH_2

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$$R_9$$
 is CH_2 N CH_2 R_{12} R_{12}

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3, and x + y + z = 3 to 300,000 and $S_1 = CO_2$ or SO_3 . In a preferred illustrative embodiment, t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1 to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

Alternatively the oligomer or polymer compound can be cationic in the surfactant head and thus have a structure such as:

20 in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

21
22
$$R_7$$
 is
$$CH_2 - CH - CH - R_{10}$$
23
24
OH OH

and in which R_{10} , R_{11} , R_{12} = H or CH₃, t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000. An especially preferred and illustrative embodiment includes an oligomer or polymer in which t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

In yet another illustrative embodiment, the oligomer or polymer can have a molecular structure that includes an anionic surfactant functional group such as:

where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

20
$$21 R_7 is$$

$$22$$

$$23$$

$$CH_2 CH-CH-R_{10}$$

$$OH OH$$

$$\begin{array}{ccc}
24 & & & & \\
25 & & R_8 \text{ is} & & & \\
\end{array}$$

in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to 300,000, and $S_1 = CO_2$ or SO_3 . In one such illustrative embodiment, it is preferred that t = 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10, 000, y = 2 to 300,000, and z = 0 to 10,000.

Further as noted above, the illustrative oligomer or polymer can have a nonionic surfactant group and preferably has a molecular structure such as:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

18
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$$R_7$$
 is

 CH_2
 $CH^-CH^-R_{10}$
20
21

$$R_8$$
 is CH_2 CH_2

26
27
$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{12}

-23-

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and in which, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000. In such instances, a preferred illustrative embodiment is achieved when t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

Fundementally the polymeric backbone can be saturated as noted in the above illustrative examples or unsaturated. In such illustrative embodiments, the oligomer or polymer has a back bone structure such as the following:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3 . As for the R_7 , R_8 and R_9 groups, these may be the same as those disclosed above. Thus one of skill in the art should appreciate that zwitterionic, cationic, anionic and nonionic surfactant groups may be attached to the unsaturated backbone structure shown above and that such compounds are illustrative of the disclosed and claimed subject matter.

As discussed above, the novel oligomers and polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic surfactant systems. The conventional viscoelastic-surfactant-based fluids useful for the claimed subject matter are those in the following references, all of which are incorporated herein by reference – Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557.

6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168,

Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322. Of these, the preferred viscoelastic-surfactant-based fluids are those based on anionic, cationic, or zwitterionic surfactants or mixtures of anionic and nonionic surfactants or mixtures of cationic and nonionic surfactants or mixtures of zwitterionic and nonionic surfactants. And of these, the particularly preferred viscoelastic-surfactant-based fluids are those based on zwitterionic surfactants or mixtures of zwitterionic and nonionic surfactants. In both the preferred viscoelastic-surfactant-based fluids, and in the particularly preferred viscoelastic-surfactant-based fluids, a minority amount of an additional surfactant, termed a "co-surfactant", such as, for example, 2-ethylhexanol or SDBS may optionally be employed. The viscoelastic oligomers or polymers of the claimed subject matter may be created in the presence of conventional viscoelastic surfactant systems or may be synthesized in separate steps, optionally processed or dried, and then subsequently admixed into a solution of conventional viscoelastic surfactants.

The aqueous well fluids made in accordance with the claimed subject matter may optionally include a sufficient quantity of at least one water-soluble inorganic salt to effect formation stability. Typically, water-soluble potassium and ammonium salts, such as potassium chloride and ammonium chloride are employed. However, other shale inhibition compounds may be utilized including organic amine based compounds and other known shale inhibition agents. Additionally, calcium chloride, calcium bromide and zinc halide salts may also be used to increase the specific gravity (i.e., the density) of the solution. Formation stability and in particular clay stability are achieved at a concentration of a few percent by weight and as such the density of the fluid is not significantly altered by the presence of the inorganic salt unless fluid density becomes an important consideration, at which point, heavier inorganic salts may be employed.

Other compounds useful in the claimed subject matter include other viscosifiers, corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, and/or weighting agents, among other additives. Some typical brine-based well fluid viscosifying additives include "natural" or biopolymers or derivatives thereof, such as, for example, xanthan gum and hydroxyethyl cellulose (HEC) or synthetic polymers and oligomers such as poly(ethylene glycol) (PEG), poly(diallyl amine), poly(acrylamide),

poly(aminomethylpropylsulfonate [AMPS]), poly(acrylonitrile), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl amine), poly(vinyl sulfonate), poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), poly(vinylpyrrolidone), poly(vinyl lactam) and co-, ter-, and quater-polymers of the following co-monomers: ethylene, butadiene, isoprene, styrene, divinylbenzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6-heptadiene-4-one (diallyl ketone), diallyl amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinylpyrrolidone, and vinyl lactam. viscosifiers include the clay-based viscosifiers, especially laponite and other small fibrous clays such as the polygorskites (attapulgite and sepiolite).

One of ordinary skill in the art should appreciate that the use of "inert" filler materials can be added to impart strength to a fluid. Examples of such materials include shredded rubber tires, shredded battery casings, peanut hulls, cotton seed hulls, woody material, and other plant fibers that should be well known to one of skill in the art.

Additional brine-based well fluid surfactant additives useful in the claimed subject matter include nonionic surfactants, such as ethoxylated nonylphenols containing about 6 to 20 moles of ethylene oxide, or alkyl polyethyleneoxyalcohols, ethoxylated linear alcohols, ethoxylated tridecyl alcohols, ethoxylated phenols such as nonylphenols and dodecylphenols and fatty dialkanol amides. Hydroxyethyl fatty amines are also classified as nonionic surfactants, although at low pH, they may take on some cationic character. Emulsifying surfactants including oil soluble surfactants, such as fatty diethanolamides, sorbitan fatty acid esters, and ethoxylated sorbitan fatty acid esters such as sorbitan monooleate and sorbitan sesqioleate, because of their limited solubility in typical brines, may however be incidentally included in the formulation of other products — polymer solutions, emulsions, or slurries, corrosion inhibitors, lubricants, solvents, or weighting agents — that are used as additives to brine-based well fluids.

Other surfactants useful in the claimed subject matter are those listed in "McCutcheon's Emulsifiers and Detergents 1999: North American Edition" (ISBN: 0944254624), incorporated herein by reference. They are classified as anionic, nonionic, amphoteric, zwitterionic, alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates,

alkylaryl sulfonic acids, amine acetates, amine oxides, amines, sulfonated amines, sulfonated amides, betaine derivatives, block polymers, carboxylated alcohols, alkylphenol ethoxylates, carboxylic acids, fatty acids, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines, ethoxylated amides, ethoxylated fatty acids, ethoxylated fatty esters, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic surfactants, imidazolines, imidazoline derivatives, isethionates, lanolin-based derivatives, lechithin, lechithin derivatives, methyl esters, monoglycerides, monoglyceride derivatives, olefin sulfonates, phosphate esters, phosphorous organic derivatives, polyethylene glycols, polymeric surfactants (polysaccharides, polyacrylic acids, polyacrylamides), propoxylated alcohols, propoxylated alkylphenols, propoxylated amines, propoxylated amides, propoxylated fatty acids, propoxylated fatty esters, proteinbased surfactants, quaternary surfactants, sarcosamine derivatives, silicone-based surfactants, soaps, sodium isethionate, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates of ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of hydrocarbons and petroleum, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, and tridecyl and dodecyl benzene sulfonic acids.

As mentioned earlier, the claimed subject matter concentrates on those micellar assemblies that are dominated by (1) one-dimensional extensions of the spherical micelle into rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, (2) two-dimensional extensions of the spherical micelle into planar micelles or, more likely, stacks of planar micelles (as in liquid crystals), or (3) vesicular micelles. Vesicular micelles may be spherical at their very centers, but each center sphere will be surrounded by a second, third, and possibly more layers of surfactants. Moving outward radially from the central sphere of surfactant molecules, each successively outer layer of surfactant molecules will be oriented oppositely from next inner-most layer. Vesicular micelles may also be rod-shaped at their very centers, but each central rod-shaped assembly will be surrounded by a second, third, and possibly more layers of surfactants. A stack of planar micelles may be thought of as the vesicular form of a single planar micelle. These concepts comprise yet another illustrative embodiment of the claimed subject matter.

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The above-mentioned embodiments may also comprise oligomers or polymers created by first carrying out a micellar polymerization to produce an oligomer or polymer, and then optionally processing or drying the product, and then subsequently admixing it into a solution of conventional surfactants — (1) non-viscoelastic or (2) non-viscoelastic and viscoelastic in nature. The micelles of the conventional surfactants would, in preferred instances, subsume the oligomers or polymers into the conventional surfactant micelles to create mixed micelles having superior viscoelastic properties in comparison to those of equivalent solutions not comprising the conventional surfactants and/or in comparison to those of equivalent solutions not comprising the oligomers or polymers.

It should also be appreciated by one of skill in the art that the claimed subject matter also relates to methods of using fluid loss control pills and similar fluids containing the compounds of the claimed subject matter, that can sustain stress conditions for extended periods of time without significant fluid loss or loss of desirable rheological properties. The stress conditions may include, for example, exposure to oil, high shear in pumping and placement, exposure to oxidizing breakers (including oxygen dissolved in the fluid), exposure to brines having high divalent cation content, high temperature, high differential pressure, low pH, extended time, and a combination of two or more of such stress conditions. These pills and fluids are advantageously applied in or in connection with drilling, drill-in, displacement, completion, hydraulic fracturing, work-over, packer fluid emplacement or maintenance, well treating, testing, or abandonment.

Exemplary viscoelastic surfactant compositions of improved stability in fluid loss control in accordance with the claimed subject matter are given in the following examples. The following examples are included to demonstrate preferred embodiments of the claimed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the claimed subject matter, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the claimed subject matter.

1.

Example 1: The oligomerization of the surfactant N-dodecene-1-yl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride:

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$[CH_2=CH(CH_2)_{18}][HO(CH_2)_2]_2CH_3N^+Cl^-$

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in an aqueous solution was achieved by joining a few of the carbon-carbon double bonds by a free radical oligomerization reaction within the micelles using the following processes. A viscoelastic surfactant solution is produced using 30 g/l of the surfactant Ndodecene-1-yl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride with 40 g/l ammonium chloride. A volume of 100 ml of the viscoelastic surfactant solution was placed in a bottle purged with oxygen-free, dry nitrogen gas to remove any dissolved After sufficient purging 10 mg of the free radical initiator 2,2'-azo(bisamidinopropane) dihydrochloride was added to the viscoelastic surfactant solution and mixed thoroughly. The surfactant solution was heated at 60°C for 30 minutes under an atmosphere of oxygen-free, dry nitrogen. The resulting oligomer can be thought of as related to oligo-ethylene, a relatively short-chained polyethylene, to which relatively long pendant surfactant groups – $[(CH_2)_{18}][HO(CH_2)_2]_2CH_3N^+Cl^-$ – are Oligomerization of the surfactant monomers in micelles resulted in the viscosity of the gel becoming largely insensitive to contact with hydrocarbon. The viscosity of the surfactant gel was not materially altered by the oligomerization of the surfactant monomers. The oligomerized surfactant gel retained its gel strength after prolonged contact with water. A volume of 50 ml of the oligomerized viscoelastic surfactant solution was blended with 50 ml of the original un- oligomerized viscoelastic surfactant solution. The resulting solution was blended with 8 volume % of n-hexane with no material reduction in the viscosity of the mixture being observed, whereas mixing only 6 volume % of n-hexane with the original un-oligomerized viscoelastic surfactant solution led to loss of essentially all viscosity in the mixture. Advantageously, therefore, compositions formed in accordance with the claimed subject matter provide viscoelastic surfactant fluids that are capable of controlling fluid loss, and that are capable of dissolving in fluid without leaving substantial amounts of residue. compositions are capable of controlling fluid loss at temperatures up to about 350°F or

- higher, and may also control fluid loss for an extended period of at least 4 days, and
- finally, do not interfere with other chemical additives commonly used in the petroleum
- 3 industry.
- Example 2: The oligomerization of the surfactant potassium octadec-1-ene-18-oate:

$CH_2 = CH(CH_2)_{16}CO_2 K^+$

in an aqueous solution was achieved using the following processes. The viscoelastic surfactant solution was formed by mixing 60 g/l potassium oleate with 60 g/l potassium chloride. A sample of 100 ml of the viscoelastic surfactant solution was purged with oxygen-free, dry nitrogen and mixed with 10 mg of the initiator 2,2'-azo(bisamidinopropane) dihydrochloride. The solution is heated at 60°C for 30 minutes under an atmosphere of oxygen-free, dry nitrogen. The resulting solution of oligomerized surfactants was about equally viscoelastic as the original monomeric solution but the observed viscoelasticity was insensitive to contact with hydrocarbon. The resulting oligomer can be thought of as related to oligo-ethylene, a relatively short-chained polyethylene, to which relatively long pendant groups – (CH₂)₁₆CO₂K⁺ – are linked. The gel formed by the oligomerized surfactant retained its viscoelasticity after prolonged contact with water. The observations led to the conclusion that the oligomer was viscoelastic in character, much as was the original un-oligomerized viscoelastic surfactant solution; but the oligomerized solution was more stable than the original un-

CH₂=CH-CH=CH-(CH₂)₁₄CO₂'K⁺

Example 3: The oligomerization of a long-chain vinyl surfactant, the potassium salt of

in a viscoelastic solution was carried out at a concentration of 60 g/l in the presence of 40 g/l ammonium chloride. The surfactant monomers were oligomerized using 10 mg of the free radical initiator 2,2'-azo(bis-amidinopropane) dihydrochloride in 100 ml of viscoelastic surfactant solution which had been purged with oxygen-free, dry nitrogen

oligomerized solution.

octadeca-1,3-diene-17-oate:

gas. The solution was heated at 60°C for 30 minutes under an atmosphere of oxygen-

2 free, dry nitrogen. The resulting oligomer can be thought of as related to oligo-butadiene,

a relatively short-chained polybutadiene, to which relatively long pendant groups -

4 (CH₂)₁₄CO₂-K⁺ – are linked. Oligomerization of the surfactant resulted in a semi-rigid

gel that retained the viscoelasticity of the original monomeric surfactant solution but

showed none of its sensitivity to contact with hydrocarbon or water. The observations

led to the conclusion that the oligomer was viscoelastic in character, much as was the

original un-oligomerized viscoelastic surfactant solution; but the oligomerized solution

9 was more stable than the original un-oligomerized solution.

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10 Example 4: Oligomers of N-(undec-11-enyl)-N,N-dimethylammonium chloride were

synthesized by linking the head groups with a branched C₉ bridge. First, 5-

methylnonane-1,8-diamine was reacted with 11-chloroundec-1-ene, CH₂=CH(CH₂)₉Cl,

and subsequently quaternized to produce the following monomer:

 $[CH_2=CH(CH_2)_9](CH_3)_2N^+CI^-[(CH_2)_4CHCH_3(CH_2)_4]N^+CI^-(CH_3)_2[(CH_2)_9CH=CH_2]_3.$

When this monomer was oligomerized, the product was a surfactant oligomer in which the N⁺Cl head groups, again, are almost completely free relative to their neighboring N⁺Cl head groups – each being linked to each other through relatively long (CH₂)₄CHCH₃(CH₂)₄ chains or to the oligo-ethylene backbone through relatively long pendant (CH₂)₉ chains.

The preparation of the monomer described above began with 5-methylnonane-1,8-diamine. This precursor was reacted with 11-chloroundec-1-ene, CH₂=CH(CH₂)₉Cl, under conditions such that each diamine group was be converted to secondary amines. In this first step in the synthesis, incompletely reacted material was separated from the disecondary amine by distillation. The small part of the 5-methylnonane-1,8-diamine that had reacted too much and had become tertiarized or quaternized at one or both ends by excessive reaction with the 11-chloroundec-1-ene were separated by fractional crystallization from the desired N,N'-di-(1-decenyl)-5-methylnonane-1,8-diamine. Finally, this product was then reacted with an excess of methylbromide and quaternized to produce the monomer stated above. The oligomerization of this monomer:

[CH₂=CH(CH₂)₉](CH₃)₂N⁺Cl⁻[(CH₂)₄CHCH₃(CH₂)₄]N⁺Cl⁻(CH₃)₂[(CH₂)₉CH=CH₂]₃

in a viscoelastic solution was carried out at a concentration of 60 g/l in the presence of 40 4 g/l ammonium chloride. A volume of 100 ml of the viscoelastic surfactant solution was 5 placed in a bottle purged with oxygen-free, dry nitrogen gas to remove any dissolved 6 After sufficient purging 10 mg of the free radical initiator 2,2'-azo(bis-7 amidinopropane) dihydrochloride was added to the viscoelastic surfactant solution and 8 9 mixed thoroughly. The surfactant solution was heated at 60°C for 30 minutes under an atmosphere of oxygen-free, dry nitrogen. Oligomerization of the surfactant monomers in 10 11 micelles resulted in the viscosity of the gel becoming largely insensitive to contact with hydrocarbon. The viscosity of the surfactant gel was not materially altered by the 12 oligomerization of the surfactant monomers. The oligomerized surfactant gel retained its 13 gel strength after prolonged contact with water. The observations led to the conclusion 14 that the oligomer was viscoelastic in character, much as was the original un-oligomerized 15 16 viscoelastic surfactant solution; but the oligomerized solution was more stable than the 17 original un-oligomerized solution. Example 5: The oligomerization of the viscoelastic surfactant monomer, the sodium salt 18 of N-N-dimethyl-N-methylcarboxylate-N-1-hepten-7-ammonium chloride, was carried 19 20

out to give oligo(1-hepten-7-quaternary-ammonio-N-N-dimethyl-N-methylcarboxylate), sodium salt. The resulting oligomer is believed to have the simplified structure as indicated below in the acid form rather than the sodium-salt form:

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$$\begin{array}{c} - \begin{bmatrix} \text{CH-CH}_2 \\ \text{CH}_2 \end{bmatrix}_{\text{X}} \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 - \begin{bmatrix} \text{CH}_2 \\ \text{CH}_2 \end{bmatrix}_{\text{X}} \\ \text{CH}_2 \\ \text{CH}_3 - \begin{bmatrix} \text{CH}_2 \\ \text{CH}_2 \end{bmatrix}_{\text{X}} \\ \text{CH}_2 \\ \text{COO} \\ \end{array}$$

in which x will have a value from about 2 to several hundred thousand, preferably from

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about 2 to several dozen, and more preferably from about 2 to perhaps 4. The monomer was prepared by the reaction of N-1-hept-6-enyl-N,N-dimethylamine with chloroacetic acid to produce N-1-hept-6-enyl-N-methylcarboxylic acid-N,N-dimethylammonium Upon neutralization with sodium hydroxide, the final product was the zwitterionic betaine which is the sodium salt of N-hexadecyl-N-carboxymethyl-N,Ndimethylammonium chloride - it has a negative charge on the carboxyl group and the sodium cation associated with it as a counter ion, and a positive charge on the quaternary amine group and the chloride anion associated with it as a counter ion. Example 6: The viscoelastic monomer, the sodium salt of N-carboxymethyl-N,Ndimethyl-N-1-hepten-7-ammonium chloride was mixed into the solution of the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles of the viscoelastic surfactant that is the sodium salt of N-hexadecyl-N-carboxymethyl-N,Ndimethylammonium chloride. This illustrative monomer, the sodium salt of Ncarboxymethyl-N,N-dimethyl-N-1-hepten-6-ammonium chloride, differs only in minor ways from the sodium salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride. Accordingly, the monomer was readily subsumed into the conventional rodshaped or spaghetti-like micelles, whereupon oligomerization was initiated to produce the

(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-

sodium

of

salt

oligo-

methylcarboxylate). This oligomer is inherently hydrophilic in its zwitterionic functional 1 groups and hydrophobic in the hydrocarbon chains that link all the zwitterionic functional 2 groups to each other. The oligomer is believed to be structurally quite similar to the 3 viscoelastic surfactant molecules in the well fluid and therefore is readily soluble in the 4 well fluid solution. the oligomers are likewise soluble or dispersible in other viscoelastic 5 surfactant solutions such as 10% XE862 (a product that is commercially available from 6 Schlumberger) solution with 0.3% SDBS in 13.5 pound per barrel CaBr₂-based brine. 7 Upon mixing the oligomer or polymer with the viscoelastic-surfactant-based fluid, the 8 oligomer or polymer is believed to be subsumed into the rod-shaped or spaghetti-like or 9 spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-10 like or spiraling-cylinder-like micelles is one or more such oligomer or polymer 11 molecules and when configured in this fashion, the oligomer or polymer molecules 12 impart greater thermal stability to the micelles, greater resistance to shear stress and other 13 stress conditions acting upon a fluid loss pill - including, for example, exposure to oil, 14 high shear in pumping and placement, high temperature, high differential pressure, and 15 low pH. 16 Example 7: In another illustrative embodiment of the claimed subject matter, a sufficient 17 quantity, about 10 volume%, of the co-monomer 1-heptene was mixed into a viscoelastic 18 solution of the sodium salt of 1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-19 propylsulfonate chloride, causing the solution to lose most or all of its viscoelastic 20 character. Then the 1-heptene was co-oligomerized with the sodium salt of 1-hepten-7-21 22 quaternary-ammonio-N,N-dimethyl-N-propylsulfonate chloride to produce oligo-(1heptene-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). 23 The resulting oligomer is believed to have the simplified structure as indicated below: 24

$$\begin{array}{c|c} \hline CH-CH_2 \\ \hline CH_2 \\$$

in which x and y will have values dependent upon the molar ratio of reactants added to the oligomerization reaction and the sum of x and y will have a value of about 2 to several hundred thousand, preferably from about 2 to several dozen, and more preferably from about 2 to ten. While this oligomer is inherently hydrophilic in its zwitterionic functional groups, there are two sources of hydrophobicity: in the 1-heptene copolymer species and in the hydrocarbon chains that link all the zwitterionic functional groups to By varying the molar ratio of the monomers present during the each other. polymerization reaction, the hydrophobicity and viscoelastic surfactant properties of the resulting oligomer and polymer may be controlled. The oligomer contains a point of structural similarity to the small molecule viscoelastic surfactants and therefore is readily soluble in such conventional viscoelastic surfactant solutions as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the oligomer with the viscoelastic-surfactant-based fluid, the oligomer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiralingcylinder-like micelles is one or more such oligomer molecules and when configured in this fashion, the oligomer molecules impart greater thermal stability to the micelles,

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greater resistance to shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to oil, high shear in pumping and placement, high temperature, high differential pressure, and low pH.

Example 8: In another illustrative embodiment of the claimed subject matter, a sufficient quantity, about 8 volume%, of the co-monomer 1-heptene was mixed into a viscoelastic solution of 1-heptene-6,7-diol and the sodium salt of 1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate chloride, causing the solution to lose most or all of its viscoelastic character. The resulting oligomer, oligo-(1-heptene-co-1-heptene-6,7-diol-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate), is believed to have the simplified structure as indicated below:

in which x, y and z will have values dependent upon the molar ratio of reactants added to the oligomerization reaction and the sum of x, y, and z will have a value of about 3 to several hundred thousand, preferably from about 3 to several dozen, and more preferably from about 3 to ten. As with the other polymers of the claimed subject matter, the above illustrative polymer is soluble in conventional viscoelastic surfactant well fluids such as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the illustrative polymer with such a viscoelastic-

surfactant-based fluid, the polymer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rodshaped or spaghetti-like or spiraling-cylinder-like micelles is one or more such polymer molecules and when configured in this fashion, the polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill - including, for example, exposure to high shear in pumping and placement, high temperature, high differential pressure, and low pH. Additionally, the co-monomer 1-heptene-6,7-diol incorporates a vicinal diol functionality into the polymer. Surface forces should cause the vicinal diol functionality to present itself at the outer surface of any rod-shaped micelle in which it has become subsumed. 10 The vicinal diol functionality was subsequently crosslinked with borate, leading effectively to the crosslinking of the viscoelastic surfactant assemblies in which the oligomers had been subsumed.

As discussed above, the novel oligomers or polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic The viscoelastic-surfactant-based fluids useful for the claimed surfactant systems. subject matter are those in the following citations, all of which are incorporated herein by reference - Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557, 6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168, Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322.

Furthermore, the oligomeric or polymeric viscoelastic surfactants may be added to a well fluid in substantially any convenient manner. Thus, the oligomeric or polymeric viscoelastic surfactants may be added directly to the well fluid either in solid form or in the form of an aqueous solution. Alternatively, the oligomeric or polymeric viscoelastic surfactants may be separately added to a solution already containing other surfactants or viscoelastic surfactants to provide a fluid loss controlling base solution, with the optional

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crosslinking agents thereafter being added to the fluid loss controlling base solution immediately prior to use.

In preferred embodiments, the oligomeric or polymeric viscoelastic surfactants, including optional crosslinking agents, are supplied to the well fluid at a level of about 20 ppm to about 20 parts per 100 parts of the well fluid, more preferably about 100 ppm to about 15 parts per 100 parts of the well fluid.

In more preferred embodiments, the oligomeric or polymeric viscoelastic surfactants, including optional crosslinking agents, are supplied to the well fluid already containing an amount of other surfactants or viscoelastic surfactants. When these more preferred embodiments are exercised, the oligomeric or polymeric viscoelastic surfactants are supplied at a level of about 20 ppmw to about 10 parts per 100 parts of the well fluid, preferably about 100 ppmw to about 5 parts per 100 parts of the well fluid.

Techniques for measuring fluid loss control are well known in the art and should be well known to one of skill and knowledge of the formulation of drilling fluids. Specifically, the fluid loss measurements of the present disclosure were made with reference to API Recommended Practice RP 13B-1, Second Edition, September 1997, pp. 9-11, the contents of which are incorporated by reference.

While the apparatus, compositions and methods of the claimed subject matter have been described in terms of preferred or illustrative embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the claimed subject matter. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the claimed subject matter.

3.

What is claimed is:

1. A wellbore fluid comprising:

an aqueous based continuous phase;

a viscoelastic surfactant; and

a surfactant-polymer compound soluble in an aqueous solution, the surfactant-polymer compound having a hydrophobic backbone and a plurality of hydrophilic functional groups attached to the hydrophobic backbone,

wherein the hydrophobic backbone is the reaction product of one or more molecules having polymerizable alkene or alkyne functional groups;

wherein the hydrophilic functional groups are selected from: zwitterionic surfactant functional groups, anionic surfactant functional groups, cationic surfactant functional groups, and nonionic surfactant functional groups; and,

wherein the combination of the viscoelastic surfactant and surfactant-polymer compound form micellar assemblies.

2. The wellbore fluid of claim 1 further comprising a water-soluble inorganic salt.

3. The wellbore fluid of claim 1 wherein the acid form of the surfactant-polymer compound has the structure:

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wherein x = 2 to 300,000.
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      4. The wellbore fluid of claim 3 wherein x = 2 to 36.
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      5. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of
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      oligo- or poly-(α-alkenyl -ω- or α-alkynyl -ω-quaternary-ammonio-N-N-dialkyl-N-
 7
      alkylcarboxylate) or a mixture further comprising a salt of N-alkyl-N-carboxymethyl-
      N,N-dimethylammonium chloride.
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      6. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of
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      oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate) or
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      a mixture further comprising a salt of N-hexadecyl-N-carboxymethyl-N,N-
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      dimethylammonium chloride.
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      7. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of
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      oligo- or poly-(\alpha-alkenyl -\omega- or \alpha-alkynyl -\omega-quaternary-ammonio-N,N-dialkyl-N-
      alkylcarboxylate).
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      8. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of
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      oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate).
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      9. A wellbore fluid comprising:
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             an aqueous fluid;
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             a viscoelastic surfactant;
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             a thickener soluble in the aqueous fluid,
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             wherein the thickener has a hydrophobic oligomeric or polymeric backbone made
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      from the reaction of alkene monomer or alkyne monomer, or mixtures thereof, and
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             wherein surfactant functional groups are attached to the hydrophobic backbone.
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      wherein the surfactant functional group is selected from: zwitterionic surfactant
      functional groups, anionic surfactant functional groups, cationic surfactant functional
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```

groups, and nonionic surfactant functional groups; and,

wherein the thickener has a molecular confirmation such that the surfactant functional groups are hydrophilic and the hydrophobic oligomeric or polymeric backbone is hydrophobic; and

wherein the combination of viscoelastic surfactant and thickener form micellar assemblies such that the wellbore fluid thickener develops viscoelastic characteristics.

10. The wellbore fluid of claim 9 wherein the thickener has the following structure:

$$\begin{array}{c|c} \hline CH-CH_2 \\ \hline CH_2 \\ CH_2 \\ \hline CH_2 \\ CH_2 \\ \hline CH$$

wherein x + y = 2 to 300,000.

12 11. The wellbore fluid of claim 10 wherein x + y = 2 to 36.

12. The wellbore fluid of claim 11 wherein the thickener is a salt of oligo- or poly-(α -alkene - ω - or α -alkyne-co- α -alkenyl - ω - or α -alkynyl - ω -quaternary-ammonio-N,N-dialkyl-N-alkylsulfonate).

1 13. The wellbore fluid of claim 11 wherein the thickener is oligo- or poly-(1-heptene-co-2

1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate).

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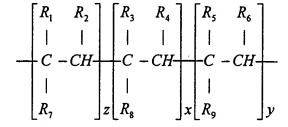
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14. The wellbore fluid of claim 9 wherein the viscoelastic surfactant is selected from the anionic, nonionic, amphoteric, zwitterionic, alcohols, alkano-lamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, amine acetates, amine oxides, amines, sulfonated amines, sulfonated amides, betaines, block polymers, carboxylated alcohols, alkylphenol ethoxylates, carboxylic acids, fatty acids, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines, ethoxylated amides, ethoxylated fatty acids, ethoxylated fatty esters, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic surfactants, imidazolines, isethionates, lanolins, methyl esters, monoglycerides, olefin sulfonates, phosphate esters, lechithins. polyethylene glycols, polysaccharides, polyacrylic acids, polyacrylamides, propoxylated alcohols, propoxylated alkylphenols, propoxylated amines, propoxylated amides, propoxylated fatty acids, propoxylated fatty esters, protein-based surfactants, quaternary surfactants, sarcosamines, silicone-based surfactants, soaps, sodium isethionate, sorbitans, sucrose and glucose esters, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates of ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of hydrocarbons and petroleum, sulfosuccinates, taurates, and tridecyl and dodecyl benzene sulfonic acids and mixtures thereof.

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15. The wellbore fluid of claim 9 wherein the thickener has the following structure: 23



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where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3 27

- wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3,
- and x + y + z = 3 to 300,000 and $S_1 = CO_2$ or SO_3 .

- 16. The wellbore fluid of claim 15 wherein t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1
- to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

- 17. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following
- structure:

wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000.

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18. The wellbore fluid of claim 17 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

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19. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure

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where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

$$\begin{array}{ccc}
6 & & & \\
7 & & R_8 \text{ is} & & & \\
& & & \\
\end{array}$$

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R₉ is
$$R_{11}$$
 R_{11}
 R_{2}
 R_{12}
 R_{12}

- wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to 300,000, and $S_1 = CO_2^-$ or SO_3^- .
- 20. The wellbore fluid of claim 19 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10, 000, y = 2 to 300,000, and z = 0 to 10,000.
- 23 21. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

28 wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_9$$
 is
 CH_2
 R_{12}
 R_{12}

- wherein, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000.
- 19 22. The wellbore fluid of claim 21 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.
- 22 23. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

26 wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{11}
 R_{12}

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wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3, and x + y + z = 3 to 300,000 and $S_1 = CO_2$ or SO_3 .

19 24. The wellbore fluid of claim 23 wherein t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1 to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

22 25. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000.

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19 28. The wellbore fluid of claim 25 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w 20 = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

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27. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

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wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to

17 300,000, and $S_1 = CO_2$ or SO_3 .

19 28. The wellbore fluid of claim 27 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1

20 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

22 29. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following

23 structure:

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wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_7$$
 is CH_2 CH CH R_{10} OH OH OH CH_2 CH_3 CH_2 CH_3 CH_3 CH_4 CH_5 CH_5 CH_6 CH_7 CH_8 CH_8 is CH_2 CH_8 C

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$$R_9$$
 is CH_2 $N-CH_2-S$
11 R_{12}

wherein, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000.

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18 30. The wellbore fluid of claim 29 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

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31. The wellbore fluid of claim 9 wherein the oligomers or polymers are crosslinked with polyvalent metal ions, formaldehyde, or glutaraldehyde.

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32. The wellbore fluid of claim 31 wherein the polyvalent metal ions are selected from the following: Fe²⁺, Cd²⁺, Co²⁺, Ca²⁺, Cu²⁺, UO₂²⁺, PbO²⁺, Al³⁺, Fe³⁺, Cr³⁺, Ce³⁺, Ti⁴⁺, Zr⁴⁺, Sn⁴⁺ and mixtures thereof.

- 28 33. A method of making a wellbore fluid comprising blending:
- an aqueous fluid phase;
- 30 a viscoelastic surfactant;
- a water-soluble inorganic salt;

an oligomer or polymer soluble in an aqueous salt solution, the oligomer or polymer comprising a hydrophobic oligomeric or polymeric backbone made from the oligomerization or polymerization of alkene or alkyne monomer groups, or mixtures thereof, the oligomer or polymer further comprising zwitterionic functional groups attached to the hydrophobic backbone, wherein the oligomer or polymer is hydrophilic in the zwitterionic functional groups and hydrophobic in the backbone hydrocarbon chain to form micellar assemblies such that the oligomers or polymers develop viscoelastic character prior to a polymerization step.

34. The method of claim 33 further comprising a polymerization step of the polymer or oligomer, then drying the product and subsequently admixing it into a solution of conventional surfactants.

35. A method of drilling a subterranean well, the method comprising:

drilling the subterranean well using a rotary drilling rig and circulating a drilling fluid in the subterranean well, wherein the drilling fluid is the wellbore fluid of claim 1.

36. A method of reducing the loss of fluid out of a subterranean well, the method comprising injecting into the subterranean well a wellbore fluid as recited in claim 1.

ABSTRACT

Compositions for increasing the thermal and pressure stability of well fluids
viscosified using viscoelastic surfactants, the compositions including an effective amount
of an oligomeric or polymeric compound that has a thermally stable backbone structure
and at least one pendent viscoelastic surfactant functional group. Preferred compositions
for increasing the stability of well fluids viscosified using monomeric viscoelastic
surfactants include an effective amount of an oligomeric or polymeric compound that has
a thermally stable backbone structure and a multiplicity of pendent viscoelastic surfactant
functional groups attached to said backbone structure through relatively long
hydrocarbon chains, 1 to 18 carbons in length.

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April 21, 2006

Ms. Kamila B. Abdur-Rahman PO Box 1603 Alief, TX 77411

Re: U.S. Patent Application No. 10/620,041

Entitled: Surfactant-Polymer Compositions for Enhancing the Stability of Viscoelastic-

Surfactant Based Fluid

Inventors: Robert Horton, Bethicia B. Prasek, Frederick Growcock, David P. Kippie,

John Vian, Kamila Abdur-Rahman, Morris Arvie

M-I L.L.C. Ref: PA-00146US

Dear Ms. Abdur-Rahman:

We write you regarding the above-referenced U.S. application in which you are listed as an inventor. In July 2003, when the application was filed, you as well as the other inventors signed the Declaration and Assignment. However, we have received a notice from the Patent Office that your signature was not dated, therefore they are requiring we submit a new declaration with a new signature and date.

We have enclosed a new Declaration for your execution as well as a copy of the application, original Declaration and Assignment you previously executed. Please sign and date the new declaration (yellow tab) and forward to us in the enclosed return FedEx envelope as soon as possible.

Please do not hesitate to contact me or Carter White at 281-561-1450 or cjwhite@miswaco.com should you have any questions. We appreciate your help with this matter.

Regards.

Patent Paralegal

Encl.

cc: Carter J. White, Ph.D.

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as Express Mail, Airbill No., in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on the date shown below.			
Dated:	Signature:0		

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SURFACTANT-POLYMER COMPOSITIONS FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED FLUID

the specification of which was filed on July 15, 2003 as Application No. 10/620,041.

In the event that the filing date and/or Application No. are not entered above at the time I execute this document, and if such information is deemed necessary, I hereby authorize and request my attorneys/agent(s) at Osha · Liang LLP, 1221 McKinney St., Suite 2800, Houston, Texas 77010, to insert above the filing date and/or Application No. of said application.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment, if any, specifically referred to herein.

I acknowledge the duty to disclose all information known to me that is material to patentability in accordance with Title 37, Code of Federal Regulations, § 1.56.

FOREIGN PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

x no such foreign applications have been filed	
such foreign application have been filed as follows:	

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Application Number	Country	Date of Filing	Priority Claimed Under 35 USC 119
	····		<u> </u>

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

Country	Date of Filing
	Country

CLAIM FOR BENEFIT OF EARLIER U.S. PROVISIONAL APPLICATIONS

I hereby claim priority benefits under Title 35, United States Code §119(e), of any United States provisional patent application(s) listed below:

no such U.S. provisional applications have been filed.

x such U.S. provisional application have been filed as follows:

Application Number	Date of Filing	Priority Claimed Under 35 USC 119
60/319,575	September 25, 2002	X Yes No

CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)

I hereby claim the benefit under Title 35, United States Code, §120 of the United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose all information that is material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56 which became available to me between the filing date of the prior application and the national or PCT international filing date of this application:

such U.S./PCT application have been filed as follows:

x no such U.S./PCT applications have been filed.

Application Number	Relationship	Parent Application	Date of Filing
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Please mail all correspondence to Jeffrey S Bergman, whose address is:

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APPLICATION FOR UNITED STATES LETTERS PATENT

for

SURFACTANT-POLYMER COMPOSITIONS FOR ENHANCING THE STABILITY OF VISCOELASTIC-SURFACTANT BASED FLUID

by

Robert L. Horton
Bethicia B. Prasek
Frederick B. Growcock
David Kippie
John W. Vian
Kamila B. Abdur-Rahman
and
Morris Arvie, Jr.

This application claims the benefit of U. S. Provisional Application No. 60/319,575, filed September 25, 2002, the entire contents of which are incorporated by reference herein.

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BACKGROUND

When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. For the purposes of the present disclosure, such a fluid will be referred to as a "well fluid." Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (i.e., drilling into a targeted formation), transportation of cuttings to the surface, controlling formation pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which a well is being drilled, fracturing the formation in the vicinity of a well, displacing the fluid within a well with another fluid, cleaning a well, testing a well, emplacing spacer or fluid loss control pills at various points in the displacement, completion, or work-over process, emplacing a packer fluid in the completed wellbore during production, preparing the well for abandonment, abandoning the well or, otherwise treating the well or the formation. A commonly used type of well fluid is based on water-based solutions including brines. Brines, such as CaBr2 brine, are commonly used as well fluids because of the ability to control the density of the solution over a wide density range. Further the brines are typically substantially free of suspended solids and brines typically do not damage the more common types of subterranean formations.

When drilling progresses to the level of penetrating a hydrocarbon-bearing formation, special care may be required to maintain the stability of the wellbore. Examples of formations in which problems often arise are highly permeable and/or poorly consolidated formation and thus a technique known as "under-reaming" may be employed. In conducting the under-reaming process, the wellbore is drilled to penetrate the hydrocarbon-bearing zone using conventional techniques. A casing generally is set in the wellbore to a point just above the hydrocarbon-bearing zone. The hydrocarbon-bearing zone then may be re-drilled to a wider diameter, for example, using an expandable under-reamer that increases the diameter of the wellbore. Under-reaming

usually is performed using special "clean" drilling fluids. Typically the "clean" drilling fluids used in under-reaming are aqueous, dense brines that are viscosified with a gelling and/or cross-linked polymer to aid in the removal of formation cuttings. The expense of such fluids limits their general use in the drilling process.

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When the target subterranean formation has a high permeability a significant quantity of the drilling fluid may be lost into the formation. Once the drilling fluid is lost into the formation, it becomes difficult to remove. Removal of the aqueous based well fluids is desired to maximize the production of the hydrocarbon in the formation. It is well known in the art that calcium- and zinc-bromide brines can form highly stable, acid insoluble compounds when reacted with the formation rock itself or with substances contained within the formation. These reactions often may substantially reduce the permeability of the formation to any subsequent out-flow of the desired hydrocarbons. As should be well known in the art, it is widely and generally accepted that the most effective way to prevent such damage to the formation is to limit fluid loss into the formation. Thus, providing effective fluid loss control is highly desirable to prevent damaging the hydrocarbon-bearing formation. For example such damage may occur during, completion, drilling, drill-in, displacement, hydraulic fracturing, work-over, packer fluid emplacement or maintenance, well treating, or testing operations.

Techniques that have been developed to control fluid loss include the use of fluid loss control "pills." As the term is used in this disclosure a "pill" is a quantity of fluid added to the well fluid so as to temporarily change the properties of the well bore fluid at or near a specific point in the well bore. Significant research has been directed to determining suitable materials for the fluid loss pills, as well as controlling and improving the properties of the fluid loss pills. Typically, fluid loss pills work by enhancing filter-cake buildup on the face of the formation to inhibit fluid flow into the formation from the wellbore; however the fluids in accordance with the claimed subject matter are effective by developing extremely high viscosity in the environment at and just within the face of the formation to inhibit fluid flow into the formation from the wellbore. Because of the high temperatures, high shear (caused by the pumping and placement of the pill), high pressures, and low pH to which well fluids may be exposed (i.e., "stress

conditions"), synthetic polymeric materials typically used to form fluid loss pills and to viscosify the well fluids tend to degrade rather quickly.

One class of viscosifiers commonly used in the petroleum industry comprises polymeric structures starting with molecular weights of hundreds of thousands to several million grams per mole. These large, chemically bonded structures are often crosslinked to further increase molecular weight and effective viscosity per gram of polymer added to the fluid. These large molecules are quite stable under the thermal conditions typically encountered in a subterranean reservoir. However, this thermal stability is believed to contribute to decreased well productivity. As a result, expensive and often corrosive breakers have been designed to destroy the molecular backbone of these polymeric structures. These breakers are typically oxidizers or enzymes and are at best only partially effective with typical reservoir cleanup less than 80% complete and more usually much less than 50% complete. It is also reported in the literature that the long term stability of polymeric based thickening agents is shortened by the high temperature, high shear, high pressures, and low pH to which well fluids may be exposed (i.e., "stress conditions").

Viscoelastic surfactants are commonly used in the petroleum industry as an alternative to the above mentioned polymeric thickening agents. Viscoelastic surfactants are relatively small molecules with each molecule being typically less than 500 grams per mole (i.e., molecular weight less than 500). These small molecules will associate under certain conditions to form structures which resemble the polymer molecules but which are not stable structures. The individual molecules of surfactant begin to associate to form rod-like or spiraling—cylinder-like micelles. These micelle structures are always in an equilibrium state of breaking and reforming. As dynamic structures, these polymer-shaped micelles are readily destroyed by shear, presence of hydrocarbons or increased temperature. While these features are desirable especially in a hydrocarbon-bearing formation, there is minimal control over the conditions under which micelle breakup occurs. Therefore, under conditions of exposure to oil, high temperature, high shear, or other "stress conditions", the viscoelastic surfactants rapidly return to their original small independent spherical micellar state. When the viscoelastic micelles are broken down to

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this small independent spherical micellar state, the desired viscous nature of the well fluid is lost. In some cases the loss is temporary, in others the loss may be more permanent.

Presently there exists an unmet need for a simple, inexpensive way to increase the thermal range for viscoelastic-surfactant-based viscosifying agents used in downhole applications. Preferably, this thermal extender would be applicable to various viscoelastic-surfactant-based viscosifying agents.

SUMMARY

Upon review of the following disclosed and claimed subject matter, one of skill in the art should appreciate and understand that one illustrative embodiment is a wellbore fluid that includes: an aqueous based continuous phase; a viscoelastic surfactant; and a surfactant-polymer compound soluble in an aqueous solution. The surfactant-polymer compound has a molecular structure including a hydrophobic backbone and a plurality of hydrophilic functional groups attached to the hydrophobic backbone. The hydrophobic backbone is the reaction product of one or more molecules having polymerizable alkene or alkyne functional groups, for example an oligo- or poly-ethylene structure. In contrast the hydrophilic functional groups can be zwitterionic surfactant functional groups, anionic surfactant functional groups, cationic surfactant functional groups, and nonionic surfactant functional groups. The illustrative embodiment is molecularly designed such that the combination of the viscoelastic surfactant and surfactant-polymer compound forms micellar assemblies in the wellbore fluid. In one illustrative and exemplary embodiment the acid form of the surfactant-polymer compound has the structure:

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in which x has a value of 2 to 300,000 and preferably x has a value of 2 to 36 Alternatively, the surfactant-polymer compound can be a salt of oligo- or poly-(α -alkenyl- ω - or α -alkynyl- ω -quaternary-ammonio-N-N-dialkyl-N-alkylcarboxylate) or a mixture further comprising a salt of N-alkyl-N-carboxymethyl-N,N-dimethylammonium chloride. Another alternative and illustrative embodiment is where the surfactant-polymer compound is a salt of oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate) or a mixture further comprising a salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride. A third alternative is where the surfactant-polymer compound is a salt of oligo- or poly-(α -alkenyl- ω - or α -alkynyl- ω -quaternary-ammonio-N,N-dialkyl-N-alkylcarboxylate), or is a salt of oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate).

 Additional embodiments of the claimed subject matter include zwitterionic surfactant heads such that the polymers or oligomers have the following structures:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_9$$
 is
 CH_2
 N
 N
 CH_2
 R_{12}
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and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 18, and x + y + z = 3 to 300,000 and $S_1 = CO_2^-$ or SO_3^- . In a preferred illustrative embodiment, t = 12 to 16, $\mu = 6$ to 12; v = 12 to 18, w = 1 to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

Alternatively the oligomer or polymer compound can be cationic in the surfactant head and thus have a structure such as:

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in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

R₈ is
$$CH_2$$
 CH_3

R₉ is CH_2 CH_3

R₉ is CH_2 CH

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000. An especially preferred and illustrative embodiment includes an oligomer or polymer in which t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

In yet another illustrative embodiment, the oligomer or polymer can have a molecular structure that includes an anionic surfactant functional group such as:

where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

$$R_8$$
 is CH_2 CH_3

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$$R_9$$
 is
 CH_2
 R_{11}
 CH_2
 R_{12}

in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to

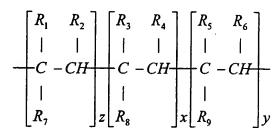
300,000, and $S_1 = CO_2$ or SO_3 . In one such illustrative embodiment, it is preferred that t

= 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10, 000, y = 2 to 300,000, and z = 0 to

10,000.

Further as noted above, the illustrative oligomer or polymer can have a nonionic

surfactant group and preferably has a molecular structure such as:



in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_7$$
 is

 CH_2
 CH
 CH
 CH
 CH
 OH
 OH

17
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$$R_8$$
 is
$$\begin{bmatrix} CH_2 \\ u \end{bmatrix}_u$$

$$R_9$$
 is
$$CH_2 \longrightarrow N - CH_2 - S_1$$

$$R_{12}$$

and in which, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000. In such instances, a preferred illustrative embodiment is achieved when t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

Fundamentally the polymeric backbone can be saturated as noted in the above illustrative examples or unsaturated. In such illustrative embodiments, the oligomer or polymer has a back bone structure such as the following:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3 . As for the R_7 , R_8 and R_9 groups, these may be the same as those disclosed above. Thus one of skill in the art should appreciate that zwitterionic, cationic, anionic and nonionic surfactant groups may be attached to the unsaturated backbone structure shown above and that such compounds are illustrative of

the disclosed and claimed subject matter.

As discussed above, the novel oligomers and polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic surfactant systems. The conventional viscoelastic-surfactant-based fluids useful for the claimed subject matter are those in the following references, all of which are incorporated herein by reference - Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557, 6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168, Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322. Of these, the preferred viscoelastic-surfactant-based fluids are those based on anionic, cationic, or zwitterionic surfactants or mixtures of anionic and nonionic surfactants or mixtures of cationic and nonionic surfactants or mixtures of zwitterionic and nonionic surfactants. And of these, the particularly preferred viscoelastic-surfactant-based fluids

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are those based on zwitterionic surfactants or mixtures of zwitterionic and nonionic surfactants. In both the preferred viscoelastic-surfactant-based fluids, and in the particularly preferred viscoelastic-surfactant-based fluids, a minority amount of an additional surfactant, termed a "co-surfactant", such as, for example, 2-ethylhexanol or SDBS may optionally be employed. The viscoelastic oligomers or polymers of the claimed subject matter may be created in the presence of conventional viscoelastic surfactant systems or may be synthesized in separate steps, optionally processed or dried, and then subsequently admixed into a solution of conventional viscoelastic surfactants.

It has been found that the oligomers or polymers of the illustrative drilling fluids can be crosslinked with polyvalent metal ions, formaldehyde, or glutaraldehyde. In one such embodiment, the polyvalent metal ions are selected from: Fe²⁺, Cd²⁺, Cd²⁺, Ca²⁺, Cu²⁺, UO₂²⁺, PbO²⁺, Al³⁺, Fe³⁺, Cr³⁺, Ce³⁺, Ti⁴⁺, Zr⁴⁺, Sn⁴⁺ and mixtures thereof.

One of skill in the art should also appreciate that the disclosed and claimed subject matter includes a method of making a wellbore fluid as is disclosed herein. In one such illustrative embodiment, the method involves the blending of an aqueous fluid phase, a viscoelastic surfactant, a water-soluble inorganic salt, and an oligomer or polymer soluble in the aqueous salt solution. The oligomer or polymer includes a hydrophobic oligomeric or polymeric backbone made from the oligomerization or polymerization of alkene or alkyne monomer groups, or mixtures thereof. The oligomer or polymer further comprises surfactant functional groups attached to the hydrophobic backbone, wherein the oligomer or polymer is hydrophilic in the surfactant functional groups and hydrophobic in the backbone hydrocarbon chain. Thus the oligomer or polymer has a molecular structure that promotes the formation of micellar assemblies such that the oligomers or polymers develop viscoelastic character prior to a polymerization step.

The claimed subject matter also encompasses a method of drilling a subterranean well as well as other sues for the wellbore fluid that should be apparent to one of skill in the art.

Further details regarding the claimed subject matter can be found in the following description.

DESCRIPTION

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The claimed subject matter relates to compositions for increasing the thermal durability of viscoelastic-surfactant-based well fluids. More specifically, the claimed subject matter relates to the fields of fluid rheology, thickeners, viscosifiers, viscoelastic fluids, viscoelastic surfactant fluids, drilling fluids, well fracturing fluids, well treatment fluids and fluid control pills. Further, the claimed subject matter relates to increasing the thermal and pressure stability of well fluids viscosified using viscoelastic surfactants by including an effective amount of a surfactant-oligomeric or surfactant-polymeric compound that has a thermally stable backbone structure and viscoelastic surfactant appendages. As the term is used in the present disclosure, "effective" simply means an amount sufficient to raise the temperature stability of the viscoelastic-surfactant based well fluid system by a measurable amount.

In accordance with one illustrative embodiment of the claimed subject matter, a sufficient quantity of at least one surfactant-oligomeric or surfactant-polymeric compound that is soluble in an aqueous salt solution is employed to affect the desired viscosity. In the claimed subject matter, the molecules of the surfactant-oligomeric or surfactant-polymeric compound have a hydrophobic oligomeric or polymeric backbone made preferably from the oligomerization or polymerization of alkene and/or alkyne groups. As the term is used herein, "thickener" and surfactant-oligomeric or surfactantpolymeric compound are used interchangeably and are intended to mean the compounds substantially described and claimed herein. The thickener of the claimed subject matter also includes chemical functional groups that are structurally similar to prior art viscoelastic surfactants and therefore these molecules exhibit similar chemical characteristics of prior art viscoelastic surfactants. Thus the hydrophobic backbone is chemically linked to and thus rendered at least in part hydrophilic by the presence of these chemical functional groups. One such illustrative compound is the product of the oligomerization reaction of a monomer such as the sodium salt of N-N-dimethyl-Nmethylcarboxylate-N-1-hepten-7-ammonium chloride to give the sodium salt of oligo-(1hepten-7-quaternary-ammonio-N-N-dimethyl-N-methylcarboxylate). The resulting oligomer is believed to have the simplified structure as indicated below in the acid form rather than the sodium-salt form:

3 about 2 to several dozen. The monomer may be prepared, for example, by the reaction of 4 methylcarboxylic acid-N,N-dimethylammonium chloride. 5

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N-hexadecyl-N,N-dimethylamine with chloroacetic acid to produce N-hexadecyl-N-Upon neutralization with

in which x will have a value from about 2 to several hundred thousand, preferably from

sodium hydroxide, the final product is the zwitterionic betaine which is the sodium salt of

N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride – it has a negative

charge on the carboxyl group and the sodium cation associated with it as a counter ion,

and a positive charge on the quaternary amine group and the chloride anion associated

with it as a counter ion. Alternatively, the sodium and chloride counter ions may be

separated therefrom, leaving the negatively charged carboxyl group and the positively

charged quaternary amine group as counter ions for each other.

The sodium salt of oligo-(1-hepten-7-quaternary-ammonio-N-N-dimethyl-Nmethylcarboxylate) is an example of a salt of oligo- or poly- $(\alpha$ -alkenyl- ω -quaternaryammonio-N-N-dialkyl-N-alkylcarboxylate). This example begins to define the terms αalkenyl - ω - and α -alkynyl - ω -, wherein the " α -" designation denotes a location at or near one end of the hydrocarbyl chain, such as, for example at the 1-, 2-, or 3- position and wherein the "ω-"designation denotes a location at or near the opposite end of the hydrocarbyl chain from the α -position, such as, for example at the very end of the hydrocarbyl chain, at one carbon group away from the very end of the hydrocarbyl chain,

1 or at two carbon groups away from the very end of the hydrocarbyl chain. An α-alkene and an α-alkyne are defined similarly. An α-alkenyl-ω-carboxylate salt and an α-2 alkynyl-ω-carboxylate salt are defined in a parallel manner. An α-alkenyl-ω-N,N,N-3 4 trialkylammonium salt and an α-alkynyl-ω-N,N,N-trialkylammonium salt are defined 5 similarly. An $\alpha,\alpha+2$ -alkadienyl- ω -carboxylate salt and an $\alpha,\alpha+2$ -alkadiynyl- ω carboxylate salt are defined in a parallel manner.

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In one illustrative embodiment, a monomer like the sodium salt of Ncarboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride could be mixed into the solution of the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles of the viscoelastic surfactant that is the sodium salt of N-hexadecyl-Ncarboxymethyl-N,N-dimethylammonium chloride. This illustrative monomer, the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride. differs only in minor ways from the sodium salt of N-hexadecyl-N-carboxymethyl-N.Ndimethylammonium chloride. Accordingly, the monomer will be readily subsumed into the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon one can take well-known steps to initiate the oligomerization or polymerization of the monomer to produce the sodium salt of oligo- or poly-(1-hepten-7quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate). This oligomer or polymer will be inherently hydrophilic in its zwitterionic functional groups and hydrophobic in the hydrocarbon chains that link all the zwitterionic functional groups to each other. The oligomer or polymer is believed to be structurally quite similar to the viscoelastic surfactant molecules in the well fluid and therefore is soluble or dispersible in the well fluid solution. Similar oligomers or polymers are likewise soluble or dispersible in other viscoelastic surfactant solutions such as 10% XE862 (a product that is commercially available from Schlumberger) solution with 0.3% sodium dodecylbenzene sulfonate (SDBS) in 13.5 pound per barrel CaBr2-based brine. Upon mixing the oligomer or polymer with the viscoelastic-surfactant-based fluid, the oligomer or polymer is believed to be subsumed into the rod-shaped or spaghetti-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiraling-cylinder-like micelles is one or more such oligomer or polymer molecules and when configured in this fashion, the oligomer or polymer molecules impart greater thermal stability to the micelles, greater resistance to

shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to oil, high shear in pumping and placement, high temperature, high differential pressure, and low pH.

Another illustrative embodiment of the compounds of the claimed subject matter includes the oligomeric or polymeric products of the co-oligomerization or co-polymerization of two different monomers such as 1-heptene and the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride. Alternatively, 1-heptene can be first co-oligomerized or co-polymerized with N,N-dimethyl-1-hepten-7-amine and in a subsequent reaction the amine groups are reacted with 1-chloro-propane-3-sulfonic acid and then caustic to produce oligo- or poly-(1-heptene-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). The resulting oligomer or polymer is believed to have the simplified structure as indicated below:

$$\begin{array}{c|c} \hline CH-CH_2 \\ \hline CH_2 \\$$

in which x and y will have values dependent upon the molar ratio of reactants added to the polymerization reaction and the sum of x and y will have a value of about 2 to several hundred thousand, preferably from about 2 to several dozen. While this oligomer or polymer will be inherently hydrophilic in its zwitterionic functional groups, there are two sources of hydrophobicity: in the 1-heptene co-oligomer or co-polymer species and in the hydrocarbon chains that link all the zwitterionic functional groups to each other. By

varying the molar ratio of the monomers present during the oligomerization or polymerization reaction, the hydrophobicity and viscoelastic surfactant properties of the resulting oligomer or polymer may be controlled. The oligomer or polymer contains a point of structural similarity to the small molecule viscoelastic surfactants and therefore is soluble or dispersible in such conventional viscoelastic surfactant solutions. Similar oligomers or polymers are likewise soluble or dispersible in the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the polymer with the viscoelastic-surfactant-based fluid, the polymer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling—cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiraling—cylinder-like micelles is one or more such polymer molecules and when configured in this fashion, the polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to oil, high shear in pumping and placement, high differential pressure, and low pH.

Yet a third illustrative embodiment of the compounds of the claimed subject matter includes the co-oligomerization or co-polymerization of three or more co-monomers. For example, one could co-oligomerize or co-polymerize 1-heptene, 1-heptene-6,7-diol and N,N-dimethyl-1-hepten-7-amine. In such an illustrative embodiment, the amine groups are reacted with 1-chloro-propane-3-sulfonic acid and then caustic to produce oligo- or poly- (1-heptene -co-1-heptene-6,7-diol -co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). The resulting oligomer or polymer is believed to have the simplified structure as indicated below:

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in which x, y and z will have values dependent upon the molar ratio of reactants added to the polymerization reaction and the sum of x, y, and z will have a value of about 3 to several hundred thousand, preferably from about 3 to several dozen. As with the other oligomers or polymers of the claimed subject matter, the above illustrative oligomer or polymer is soluble or dispersible in conventional viscoelastic surfactant well fluids such as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the illustrative oligomer or polymer with such a viscoelastic-surfactant-based fluid, the oligomer or polymer is believed to be subsumed into the rod-shaped spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped spaghetti-like or spiraling-cylinder-like micelles is one or more such oligomer or polymer molecules and when configured in this fashion, the oligomer or polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill - including, for example, exposure to oil, high shear in pumping and placement, high differential pressure, and low pH. Additionally, the co-monomer 1-heptene-6,7-diol incorporates a vicinal diol functionality into the oligomer or polymer. Surface forces should cause the

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vicinal diol functionality to present itself at the outer surface of any rod-shaped micelle in which it has become subsumed.

The vicinal diol functionality provides the chemical functional group that renders the oligomers or polymers readily crosslinkable with polyvalent metal ions or complexes such as, for example, a borate, titanate, or zirconate crosslinker as taught in U. S. Patent 5,062,969, (2) divalent, trivalent, or tetravalent cations such as, for example, Fe²⁺, Cd²⁺, Co²⁺, Ca²⁺, Cu²⁺, UO₂²⁺, PbO²⁺, Al³⁺, Fe³⁺, Cr³⁺, Ce³⁺, Ti⁴⁺, Zr⁴⁺, Sn⁴⁺, and the like, (3) complexes of or other moieties containing the crosslinkers listed above in the first two categories, such as, for example, the tetrammine complex of the Cu²⁺ cation, the carbonate anion complexes of the UO₂²⁺ cation, UO₂(CO₃)₂²⁻ and UO₂(CO₃)₃⁴⁻, or the triethanolamine complex of the Ti⁴⁺ cation, (4) so-called "organic crosslinkers" such as, for example, formaldehyde, and glutaraldehyde, and (5) mixtures of the crosslinkers listed above in the first four categories and/or reaction products therefrom. Thus it is contemplated that one of skill in the art could, if desired, crosslink the illustrative oligomers or polymers with polyvalent metal ions, complexes, organic crosslinkers, or mixtures thereof, as described above. This is believed to lead effectively to the crosslinking of the viscoelastic surfactant assemblies in which the oligomers or polymers have been subsumed.

One of skill in the art should at this point appreciate that the co-oligomerization or co-polymerization reactions disclosed above result in the random placement of each co-monomer along the vinyl backbone of the illustrative oligomers or polymers. However, it is contemplated that block co-oligomerization or co-polymerization could also be used to achieve substantially similar results. Alternatively, block co-oligomerization or co-polymerization could also be used to carefully tailor the properties of the resulting oligomers or polymers made in accordance with the claimed subject matter. One of skill in the art should understand and appreciate that by systematically controlling the molar ratio of and concentration of monomers present in during the oligomerization or polymerization process, the order of addition, the temperature and duration of oligomerization or polymerzation and the initiators and catalysts used and their concentrations, the properties of the compounds of the claimed subject matter can be carefully controlled and tailored.

Other oligomers or polymers formulated in accordance with and illustrative of the claimed subject matter include such oligomers or polymers as oligo- or poly-(N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-(N,N-diallyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-(1-butene-co-N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly- (1-butene-co-1-pentene-4,5-diol- co-N-carboxymethyl-N,N-diallyl-N-methyl ammonium chloride), oligo- or poly-alkenyl or -alkynyl DMAPA amides (see Figure below), oligo- or poly-alkenyl or -alkynyl DMAPA quats, and oligo- or poly-alkenyl or -alkynyl tallow amine quaternary amines such as

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C₁₂₋₂₂ DMAPA Amide Quaternary Amine

Tallow Amine Quaternary Amine

and the like.

Except for the oligo- or poly-alkenyl or -alkynyl DMAPA amides, oligo- or poly-alkenyl or -alkynyl DMAPA quaternary amines, and oligo- or poly-alkenyl or -alkynyl tallow amine quaternary amines, oligomers or polymers of this type may be unlike those of the previous illustrative embodiments of the claimed subject matter in that they are probably not capable of effectively vacuuming up the micelles and packing them about themselves until there are enough surfactant molecules present in the vicinity of the oligomer or polymer molecule so that the spherical micelles can merge into a single rod-shaped or spaghetti-like or spiraling—cylinder-like micelles with the oligomer or polymer molecule subsumed within the rod-shaped or spaghetti-like or spiraling—cylinder-like micelles. Polymers or oligomers in accordance with the present illustrative embodiment

of the claimed subject matter are designed to be compatible with CaBr₂-, CaBr₂/CaCl₂-, ZnBr₂/CaBr₂-, and ZnBr₂/CaBr₂/CaCl₂-based brines.

Other oligomers or polymers formulated in accordance with and illustrative of the claimed subject matter include oligomers or polymers such as oligo- or poly-(ethyleneco-N,N-diallyl-N,N-dimethyl ammonium chloride), oligo- or poly-(1-butene-co-N,Ndiallyl-N,N-dimethyl ammonium chloride), oligo- or poly-(1-butene-co-1-pentene-4,5diol-co-N,N-diallyl-N,N-dimethyl ammonium chloride), and the like. oligomers of this type are probably not sufficiently compatible with CaBr₂-, CaBr₂/CaCl₂-, ZnBr₂/CaBr₂-, and ZnBr₂/CaBr₂/CaCl₂-based brines; however, they expand the scope of the claimed subject matter into useful dimensions to the extent that these polymers should be quite compatible with NaCl-, NaBr-, NaBr/NaCl-, CsBr/KBr-, and CsBr/KBr/NaCl-based brines and the like. Poly-or oligo-(1-butene-co-1-pentene-4,5-diol-co-N,N-diallyl-N,N-dimethyl ammonium chloride) incorporates a vicinal diol functionality, and so one of skill in the art should appreciate that this polymer or oligomer may be crosslinkable with polyvalent metal ions as disclosed above. As noted above. when the oligomers or polymers are crosslinked with polyvalent metal ions, we also effectively crosslink the viscoelastic surfactant assemblies in which the oligomers or polymers have been subsumed.

Additional embodiments of the claimed subject matter include zwitterionic surfactant heads such that the polymers or oligomers have the following structures:

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in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{11}
 R_{12}

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3, and x + y + z = 3 to 300,000 and $S_1 = CO_2$ or SO_3 . In a preferred illustrative embodiment, t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1 to 3, x = 0 to 10,000, y = 2 to

300,000 and z = 0 to 10,000

> Alternatively the oligomer or polymer compound can be cationic in the surfactant head and thus have a structure such as:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

and in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000. An especially preferred and illustrative embodiment includes an oligomer or polymer in which t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

In yet another illustrative embodiment, the oligomer or polymer can have a molecular structure that includes an anionic surfactant functional group such as:

where R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

R₉ is
$$CH_2$$
 R_{11}
 CH_2
 R_{12}
 R_{12}

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8 in which R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to

300,000, and $S_1 = CO_2^-$ or SO_3^- . In one such illustrative embodiment, it is preferred that t

10 = 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10, 000, y = 2 to 300,000, and z = 0 to

11 10,000.

12 Further as noted above, the illustrative oligomer or polymer can have a nonionic

surfactant group and preferably has a molecular structure such as:

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in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

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$$R_9$$
 is
 CH_2
 R_{11}
 R_{12}
 R_{12}
 R_{12}

H: 531869(B##501!.DOC)

and in which, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000. In such instances, a preferred illustrative embodiment is achieved when t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

Fundementally the polymeric backbone can be saturated as noted in the above illustrative examples or unsaturated. In such illustrative embodiments, the oligomer or polymer has a back bone structure such as the following:

in which R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3 . As for the R_7 , R_8 and R_9 groups, these may be the same as those disclosed above. Thus one of skill in the art should appreciate that zwitterionic, cationic, anionic and nonionic surfactant groups may be attached to the unsaturated backbone structure shown above and that such compounds are illustrative of the disclosed and claimed subject matter.

As discussed above, the novel oligomers and polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic surfactant systems. The conventional viscoelastic-surfactant-based fluids useful for the claimed subject matter are those in the following references, all of which are incorporated herein by reference – Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557, 6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168,

Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322. Of these, the preferred viscoelastic-surfactant-based fluids are those based on anionic, cationic, or zwitterionic surfactants or mixtures of anionic and nonionic surfactants or mixtures of cationic and nonionic surfactants or mixtures of zwitterionic and nonionic surfactants. And of these, the particularly preferred viscoelastic-surfactant-based fluids are those based on zwitterionic surfactants or mixtures of zwitterionic and nonionic surfactants. In both the preferred viscoelastic-surfactant-based fluids, and in the particularly preferred viscoelastic-surfactant-based fluids, a minority amount of an additional surfactant, termed a "co-surfactant", such as, for example, 2-ethylhexanol or SDBS may optionally be employed. The viscoelastic oligomers or polymers of the claimed subject matter may be created in the presence of conventional viscoelastic surfactants systems or may be synthesized in separate steps, optionally processed or dried, and then subsequently admixed into a solution of conventional viscoelastic surfactants.

The aqueous well fluids made in accordance with the claimed subject matter may optionally include a sufficient quantity of at least one water-soluble inorganic salt to effect formation stability. Typically, water-soluble potassium and ammonium salts, such as potassium chloride and ammonium chloride are employed. However, other shale inhibition compounds may be utilized including organic amine based compounds and other known shale inhibition agents. Additionally, calcium chloride, calcium bromide and zinc halide salts may also be used to increase the specific gravity (i.e., the density) of the solution. Formation stability and in particular clay stability are achieved at a concentration of a few percent by weight and as such the density of the fluid is not significantly altered by the presence of the inorganic salt unless fluid density becomes an important consideration, at which point, heavier inorganic salts may be employed.

Other compounds useful in the claimed subject matter include other viscosifiers, corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, and/or weighting agents, among other additives. Some typical brine-based well fluid viscosifying additives include "natural" or biopolymers or derivatives thereof, such as, for example, xanthan gum and hydroxyethyl cellulose (HEC) or synthetic polymers and oligomers such as poly(ethylene glycol) (PEG), poly(diallyl amine), poly(acrylamide),

poly(aminomethylpropylsulfonate [AMPS]), poly(acrylonitrile), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl amine), poly(vinyl sulfonate), poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), poly(vinylpyrrolidone), poly(vinyl lactam) and co-, ter-, and quater-polymers of the following co-monomers: ethylene, butadiene, isoprene, styrene, divinylbenzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6-heptadiene-4-one (diallyl ketone), dially amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinylpyrrolidone, and vinyl lactam. viscosifiers include the clay-based viscosifiers, especially laponite and other small fibrous clays such as the polygorskites (attapulgite and sepiolite).

One of ordinary skill in the art should appreciate that the use of "inert" filler materials can be added to impart strength to a fluid. Examples of such materials include shredded rubber tires, shredded battery casings, peanut hulls, cotton seed hulls, woody material, and other plant fibers that should be well known to one of skill in the art.

Additional brine-based well fluid surfactant additives useful in the claimed subject matter include nonionic surfactants, such as ethoxylated nonylphenols containing about 6 to 20 moles of ethylene oxide, or alkyl polyethyleneoxyalcohols, ethoxylated linear alcohols, ethoxylated tridecyl alcohols, ethoxylated phenols such as nonylphenols and dodecylphenols and fatty dialkanol amides. Hydroxyethyl fatty amines are also classified as nonionic surfactants, although at low pH, they may take on some cationic character. Emulsifying surfactants including oil soluble surfactants, such as fatty diethanolamides, sorbitan fatty acid esters, and ethoxylated sorbitan fatty acid esters such as sorbitan monooleate and sorbitan sesqioleate, because of their limited solubility in typical brines, may however be incidentally included in the formulation of other products – polymer solutions, emulsions, or slurries, corrosion inhibitors, lubricants, solvents, or weighting agents – that are used as additives to brine-based well fluids.

Other surfactants useful in the claimed subject matter are those listed in "McCutcheon's Emulsifiers and Detergents 1999: North American Edition" (ISBN: 0944254624), incorporated herein by reference. They are classified as anionic, nonionic, amphoteric, zwitterionic, alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates,

alkylaryl sulfonic acids, amine acetates, amine oxides, amines, sulfonated amines, sulfonated amides, betaine derivatives, block polymers, carboxylated alcohols, alkylphenol ethoxylates, carboxylic acids, fatty acids, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines, ethoxylated amides, ethoxylated fatty acids, ethoxylated fatty esters, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic surfactants, imidazolines, imidazoline derivatives, isethionates, lanolin-based derivatives, lechithin, lechithin derivatives, methyl esters, monoglycerides, monoglyceride derivatives, olefin sulfonates, phosphate esters, phosphorous organic derivatives, polyethylene glycols, polymeric surfactants (polysaccharides, polyacrylic acids, polyacrylamides), propoxylated alcohols, propoxylated alkylphenols, propoxylated amines, propoxylated amides, propoxylated fatty acids, propoxylated fatty esters, proteinbased surfactants, quaternary surfactants, sarcosamine derivatives, silicone-based surfactants, soaps, sodium isethionate, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates of ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of hydrocarbons and petroleum, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, and tridecyl and dodecyl benzene sulfonic acids.

As mentioned earlier, the claimed subject matter concentrates on those micellar assemblies that are dominated by (1) one-dimensional extensions of the spherical micelle into rod-shaped or spaghetti-like or spiraling—cylinder-like micelles, (2) two-dimensional extensions of the spherical micelle into planar micelles or, more likely, stacks of planar micelles (as in liquid crystals), or (3) vesicular micelles. Vesicular micelles may be spherical at their very centers, but each center sphere will be surrounded by a second, third, and possibly more layers of surfactants. Moving outward radially from the central sphere of surfactant molecules, each successively outer layer of surfactant molecules will be oriented oppositely from next inner-most layer. Vesicular micelles may also be rod-shaped at their very centers, but each central rod-shaped assembly will be surrounded by a second, third, and possibly more layers of surfactants. A stack of planar micelles may be thought of as the vesicular form of a single planar micelle. These concepts comprise yet another illustrative embodiment of the claimed subject matter.

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The above-mentioned embodiments may also comprise oligomers or polymers created by first carrying out a micellar polymerization to produce an oligomer or polymer, and then optionally processing or drying the product, and then subsequently admixing it into a solution of conventional surfactants – (1) non-viscoelastic or (2) non-viscoelastic and viscoelastic in nature. The micelles of the conventional surfactants would, in preferred instances, subsume the oligomers or polymers into the conventional surfactant micelles to create mixed micelles having superior viscoelastic properties in comparison to those of equivalent solutions not comprising the conventional surfactants and/or in comparison to those of equivalent solutions not comprising the oligomers or polymers.

It should also be appreciated by one of skill in the art that the claimed subject matter also relates to methods of using fluid loss control pills and similar fluids containing the compounds of the claimed subject matter, that can sustain stress conditions for extended periods of time without significant fluid loss or loss of desirable rheological properties. The stress conditions may include, for example, exposure to oil, high shear in pumping and placement, exposure to oxidizing breakers (including oxygen dissolved in the fluid), exposure to brines having high divalent cation content, high temperature, high differential pressure, low pH, extended time, and a combination of two or more of such stress conditions. These pills and fluids are advantageously applied in or in connection with drilling, drill-in, displacement, completion, hydraulic fracturing, work-over, packer fluid emplacement or maintenance, well treating, testing, or abandonment.

Exemplary viscoelastic surfactant compositions of improved stability in fluid loss control in accordance with the claimed subject matter are given in the following examples. The following examples are included to demonstrate preferred embodiments of the claimed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the claimed subject matter, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the claimed subject matter.

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Example 1: The oligomerization of the surfactant N-dodecene-1-yl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride:

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$[CH_2=CH(CH_2)_{18}][HO(CH_2)_2]_2CH_3N^+Cl^-$

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in an aqueous solution was achieved by joining a few of the carbon-carbon double bonds by a free radical oligomerization reaction within the micelles using the following processes. A viscoelastic surfactant solution is produced using 30 g/l of the surfactant Ndodecene-1-yl-N,N-bis(2-hydroxyethyl)-N-methylammonium chloride with 40 ammonium chloride. A volume of 100 ml of the viscoelastic surfactant solution was placed in a bottle purged with oxygen-free, dry nitrogen gas to remove any dissolved oxygen. After sufficient purging 10 mg of the free radical initiator 2,2'-azo(bisamidinopropane) dihydrochloride was added to the viscoelastic surfactant solution and mixed thoroughly. The surfactant solution was heated at 60°C for 30 minutes under an atmosphere of oxygen-free, dry nitrogen. The resulting oligomer can be thought of as related to oligo-ethylene, a relatively short-chained polyethylene, to which relatively long groups - $[(CH_2)_{18}][HO(CH_2)_2]_2CH_3N^+Cl^-$ - are linked. surfactant pendant Oligomerization of the surfactant monomers in micelles resulted in the viscosity of the gel becoming largely insensitive to contact with hydrocarbon. The viscosity of the surfactant gel was not materially altered by the oligomerization of the surfactant monomers. The oligomerized surfactant gel retained its gel strength after prolonged contact with water. A volume of 50 ml of the oligomerized viscoelastic surfactant solution was blended with 50 ml of the original un-oligomerized viscoelastic surfactant solution. The resulting solution was blended with 8 volume % of n-hexane with no material reduction in the viscosity of the mixture being observed, whereas mixing only 6 volume % of n-hexane with the original un-oligomerized viscoelastic surfactant solution led to loss of essentially all viscosity in the mixture. Advantageously, therefore, compositions formed in accordance with the claimed subject matter provide viscoelastic surfactant fluids that are capable of controlling fluid loss, and that are capable of dissolving in fluid without leaving substantial amounts of residue. Further, the compositions are capable of controlling fluid loss at temperatures up to about 350°F or higher, and may also control fluid loss for an extended period of at least 4 days, and

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- 2 finally, do not interfere with other chemical additives commonly used in the petroleum
- 3 industry.
- 4 Example 2: The oligomerization of the surfactant potassium octadec-1-ene-18-oate:

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 $CH_2=CH(CH_2)_{16}CO_2 K^+$

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in an aqueous solution was achieved using the following processes. The viscoelastic surfactant solution was formed by mixing 60 g/l potassium oleate with 60 g/l potassium chloride. A sample of 100 ml of the viscoelastic surfactant solution was purged with oxygen-free, dry nitrogen and mixed with 10 mg of the initiator 2.2'azo(bisamidinopropane) dihydrochloride. The solution is heated at 60°C for 30 minutes under an atmosphere of oxygen-free, dry nitrogen. The resulting solution of oligomerized surfactants was about equally viscoelastic as the original monomeric solution but the observed viscoelasticity was insensitive to contact with hydrocarbon. The resulting oligomer can be thought of as related to oligo-ethylene, a relatively shortchained polyethylene, to which relatively long pendant groups – $(CH_2)_{16}CO_2$ K⁺ – are linked. The gel formed by the oligomerized surfactant retained its viscoelasticity after prolonged contact with water. The observations led to the conclusion that the oligomer was viscoelastic in character, much as was the original un-oligomerized viscoelastic surfactant solution; but the oligomerized solution was more stable than the original unoligomerized solution.

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CH₂=CH-CH=CH-(CH₂)₁₄CO₂K⁺

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in a viscoelastic solution was carried out at a concentration of 60 g/l in the presence of 40 g/l ammonium chloride. The surfactant monomers were oligomerized using 10 mg of the free radical initiator 2,2'-azo(bis-amidinopropane) dihydrochloride in 100 ml of viscoelastic surfactant solution which had been purged with oxygen-free, dry nitrogen

Example 3: The oligomerization of a long-chain vinyl surfactant, the potassium salt of

octadeca-1,3-diene-17-oate:

gas. The solution was heated at 60°C for 30 minutes under an atmosphere of oxygen-

free, dry nitrogen. The resulting oligomer can be thought of as related to oligo-butadiene,

a relatively short-chained polybutadiene, to which relatively long pendant groups -

(CH₂)₁₄CO₂K⁺ - are linked. Oligomerization of the surfactant resulted in a semi-rigid

gel that retained the viscoelasticity of the original monomeric surfactant solution but

showed none of its sensitivity to contact with hydrocarbon or water. The observations

led to the conclusion that the oligomer was viscoelastic in character, much as was the

original un-oligomerized viscoelastic surfactant solution; but the oligomerized solution

9 was more stable than the original un-oligomerized solution.

and subsequently quaternized to produce the following monomer:

Example 4: Oligomers of N-(undec-11-enyl)-N,N-dimethylammonium chloride were synthesized by linking the head groups with a branched C₉ bridge. First, 5methylnonane-1,8-diamine was reacted with 11-chloroundec-1-ene, CH₂=CH(CH₂)₉Cl,

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 $[CH_2=CH(CH_2)_9](CH_3)_2N^+Cl^-[(CH_2)_4CHCH_3(CH_2)_4]N^+Cl^-(CH_3)_2[(CH_2)_9CH=CH_2]_3.$

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When this monomer was oligomerized, the product was a surfactant oligomer in which the N⁺Cl⁻ head groups, again, are almost completely free relative to their neighboring N⁺Cl⁻ head groups – each being linked to each other through relatively long (CH₂)₄CHCH₃(CH₂)₄ chains or to the oligo-ethylene backbone through relatively long pendant (CH₂)₉ chains.

The preparation of the monomer described above began with 5-methylnonane-1,8-diamine. This precursor was reacted with 11-chloroundec-1-ene, CH₂=CH(CH₂)₉Cl, under conditions such that each diamine group was be converted to secondary amines. In this first step in the synthesis, incompletely reacted material was separated from the disecondary amine by distillation. The small part of the 5-methylnonane-1,8-diamine that had reacted too much and had become tertiarized or quaternized at one or both ends by excessive reaction with the 11-chloroundec-1-ene were separated by fractional crystallization from the desired N,N'-di-(1-decenyl)-5-methylnonane-1,8-diamine. Finally, this product was then reacted with an excess of methylbromide and quaternized to produce the monomer stated above. The oligomerization of this monomer:

[CH₂=CH(CH₂)₉](CH₃)₂N⁺Cl⁻[(CH₂)₄CHCH₃(CH₂)₄]N⁺Cl⁻(CH₃)₂[(CH₂)₉CH=CH₂]₃

4 in a viscoelastic solution was carried out at a concentration of 60 g/l in the presence of 40 g/l ammonium chloride. A volume of 100 ml of the viscoelastic surfactant solution was 5 placed in a bottle purged with oxygen-free, dry nitrogen gas to remove any dissolved 6 After sufficient purging 10 mg of the free radical initiator 2,2'-azo(bis-7 amidinopropane) dihydrochloride was added to the viscoelastic surfactant solution and 8 mixed thoroughly. The surfactant solution was heated at 60°C for 30 minutes under an 9 atmosphere of oxygen-free, dry nitrogen. Oligomerization of the surfactant monomers in 10 11 micelles resulted in the viscosity of the gel becoming largely insensitive to contact with hydrocarbon. The viscosity of the surfactant gel was not materially altered by the 12 13 oligomerization of the surfactant monomers. The oligomerized surfactant gel retained its gel strength after prolonged contact with water. The observations led to the conclusion 14 15 that the oligomer was viscoelastic in character, much as was the original un-oligomerized viscoelastic surfactant solution; but the oligomerized solution was more stable than the 16 17 original un-oligomerized solution.

of N-N-dimethyl-N-methylcarboxylate-N-1-hepten-7-ammonium chloride, was carried out to give oligo(1-hepten-7-quaternary-ammonio-N-N-dimethyl-N-methylcarboxylate), sodium salt. The resulting oligomer is believed to have the simplified structure as indicated below in the acid form rather than the sodium-salt form:

Example 5: The oligomerization of the viscoelastic surfactant monomer, the sodium salt

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in which x will have a value from about 2 to several hundred thousand, preferably from about 2 to several dozen, and more preferably from about 2 to perhaps 4. The monomer was prepared by the reaction of N-1-hept-6-enyl-N,N-dimethylamine with chloroacetic acid to produce N-1-hept-6-enyl-N-methylcarboxylic acid-N,N-dimethylammonium chloride. Upon neutralization with sodium hydroxide, the final product was the zwitterionic betaine which is the sodium salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride – it has a negative charge on the carboxyl group and the sodium cation associated with it as a counter ion, and a positive charge on the quaternary amine group and the chloride anion associated with it as a counter ion.

Example 6: The viscoelastic monomer, the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-7-ammonium chloride was mixed into the solution of the conventional rod-shaped or spaghetti-like or spiraling-cylinder-like micelles of the viscoelastic surfactant that is the sodium salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride. This illustrative monomer, the sodium salt of N-carboxymethyl-N,N-dimethyl-N-1-hepten-6-ammonium chloride, differs only in minor ways from the sodium salt of N-hexadecyl-N-carboxymethyl-N,N-dimethylammonium chloride. Accordingly, the monomer was readily subsumed into the conventional rod-shaped or spaghetti-like micelles, whereupon oligomerization was initiated to produce the sodium salt of oligo- (1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-

methylcarboxylate). This oligomer is inherently hydrophilic in its zwitterionic functional 1 groups and hydrophobic in the hydrocarbon chains that link all the zwitterionic functional 2 groups to each other. The oligomer is believed to be structurally quite similar to the 3 viscoelastic surfactant molecules in the well fluid and therefore is readily soluble in the 4 well fluid solution. the oligomers are likewise soluble or dispersible in other viscoelastic 5 surfactant solutions such as 10% XE862 (a product that is commercially available from 6 Schlumberger) solution with 0.3% SDBS in 13.5 pound per barrel CaBr₂-based brine. 7 8 Upon mixing the oligomer or polymer with the viscoelastic-surfactant-based fluid, the oligomer or polymer is believed to be subsumed into the rod-shaped or spaghetti-like or 9 spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-10 like or spiraling-cylinder-like micelles is one or more such oligomer or polymer 11 molecules and when configured in this fashion, the oligomer or polymer molecules 12 impart greater thermal stability to the micelles, greater resistance to shear stress and other 13 stress conditions acting upon a fluid loss pill - including, for example, exposure to oil, 14 high shear in pumping and placement, high temperature, high differential pressure, and 15 16 low pH. Example 7: In another illustrative embodiment of the claimed subject matter, a sufficient 17 quantity, about 10 volume%, of the co-monomer 1-heptene was mixed into a viscoelastic 18 solution of the sodium salt of 1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-19 propylsulfonate chloride, causing the solution to lose most or all of its viscoelastic 20 character. Then the 1-heptene was co-oligomerized with the sodium salt of 1-hepten-7-21 quaternary-ammonio-N,N-dimethyl-N-propylsulfonate chloride to produce oligo-(1-22 The heptene-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate). 23 resulting oligomer is believed to have the simplified structure as indicated below: 24

$$\begin{array}{c|c} \hline \text{CH-CH}_2 \\ \hline \text{CH}_2 \\ \hline \text{CH$$

in which x and y will have values dependent upon the molar ratio of reactants added to the oligomerization reaction and the sum of x and y will have a value of about 2 to several hundred thousand, preferably from about 2 to several dozen, and more preferably from about 2 to ten. While this oligomer is inherently hydrophilic in its zwitterionic functional groups, there are two sources of hydrophobicity: in the 1-heptene copolymer species and in the hydrocarbon chains that link all the zwitterionic functional groups to each other. By varying the molar ratio of the monomers present during the polymerization reaction, the hydrophobicity and viscoelastic surfactant properties of the resulting oligomer and polymer may be controlled. The oligomer contains a point of structural similarity to the small molecule viscoelastic surfactants and therefore is readily soluble in such conventional viscoelastic surfactant solutions as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the oligomer with the viscoelastic-surfactant-based fluid, the oligomer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiralingcylinder-like micelles is one or more such oligomer molecules and when configured in this fashion, the oligomer molecules impart greater thermal stability to the micelles,

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greater resistance to shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to oil, high shear in pumping and placement, high temperature, high differential pressure, and low pH.

Example 8: In another illustrative embodiment of the claimed subject matter, a sufficient quantity, about 8 volume%, of the co-monomer 1-heptene was mixed into a viscoelastic solution of 1-heptene-6,7-diol and the sodium salt of 1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate chloride, causing the solution to lose most or all of its viscoelastic character. The resulting oligomer, oligo-(1-heptene-co-1-heptene-6,7-diol-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate), is believed to have the simplified structure as indicated below:

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in which x, y and z will have values dependent upon the molar ratio of reactants added to the oligomerization reaction and the sum of x, y, and z will have a value of about 3 to several hundred thousand, preferably from about 3 to several dozen, and more preferably from about 3 to ten. As with the other polymers of the claimed subject matter, the above illustrative polymer is soluble in conventional viscoelastic surfactant well fluids such as the 10% XE862 solution with 0.3% SDBS in 13.5 pounds per gallon CaBr₂-based brine discussed above. Upon admixing the illustrative polymer with such a viscoelastic-

surfactant-based fluid, the polymer is believed to be subsumed into the rod-shaped or spaghetti-like or spiraling-cylinder-like micelles, whereupon, sitting inside these rod-shaped or spaghetti-like or spiraling-cylinder-like micelles is one or more such polymer molecules and when configured in this fashion, the polymer molecules impart greater thermal stability to the micelles, greater resistance to shear stress and other stress conditions acting upon a fluid loss pill – including, for example, exposure to high shear in pumping and placement, high temperature, high differential pressure, and low pH. Additionally, the co-monomer 1-heptene-6,7-diol incorporates a vicinal diol functionality into the polymer. Surface forces should cause the vicinal diol functionality to present itself at the outer surface of any rod-shaped micelle in which it has become subsumed. The vicinal diol functionality was subsequently crosslinked with borate, leading effectively to the crosslinking of the viscoelastic surfactant assemblies in which the oligomers had been subsumed.

As discussed above, the novel oligomers or polymers taught in accordance with the claimed subject matter contain chemical functional groups that are similar to those found in conventional viscoelastic surfactants and thus are highly compatible with conventional viscoelastic surfactant systems. Accordingly, the claimed subject matter teaches blends of the viscoelastic oligomers or polymers with conventional viscoelastic surfactant systems. The viscoelastic-surfactant-based fluids useful for the claimed subject matter are those in the following citations, all of which are incorporated herein by reference – Canadian Patent 1,298,697, U. S. Patents 4,615,825, 4,695,389, 4,725,372, 5,258,137, 5,551,516, 5,691,292, 5,964,295, 5,965,502, 5,979,555, 5,979,557, 6,140,277, 6,194,355, 6,194,356, 6,211,120, 6,232,274, 6,239,183, Paper SPE 17,168, Paper SPE 30,098, Paper SPE 30,114, Paper SPE 30,458, Paper SPE 31,114, Paper SPE 38,622, Paper SPE 56,467, Paper SPE 57,432, Paper SPE 59,478, and Paper SPE 60,322.

Furthermore, the oligomeric or polymeric viscoelastic surfactants may be added to a well fluid in substantially any convenient manner. Thus, the oligomeric or polymeric viscoelastic surfactants may be added directly to the well fluid either in solid form or in the form of an aqueous solution. Alternatively, the oligomeric or polymeric viscoelastic surfactants may be separately added to a solution already containing other surfactants or viscoelastic surfactants to provide a fluid loss controlling base solution, with the optional

crosslinking agents thereafter being added to the fluid loss controlling base solution immediately prior to use.

In preferred embodiments, the oligomeric or polymeric viscoelastic surfactants, including optional crosslinking agents, are supplied to the well fluid at a level of about 20 ppm to about 20 parts per 100 parts of the well fluid, more preferably about 100 ppm to about 15 parts per 100 parts of the well fluid.

In more preferred embodiments, the oligomeric or polymeric viscoelastic surfactants, including optional crosslinking agents, are supplied to the well fluid already containing an amount of other surfactants or viscoelastic surfactants. When these more preferred embodiments are exercised, the oligomeric or polymeric viscoelastic surfactants are supplied at a level of about 20 ppmw to about 10 parts per 100 parts of the well fluid, preferably about 100 ppmw to about 5 parts per 100 parts of the well fluid.

Techniques for measuring fluid loss control are well known in the art and should be well known to one of skill and knowledge of the formulation of drilling fluids. Specifically, the fluid loss measurements of the present disclosure were made with reference to API Recommended Practice RP 13B-1, Second Edition, September 1997, pp. 9-11, the contents of which are incorporated by reference.

While the apparatus, compositions and methods of the claimed subject matter have been described in terms of preferred or illustrative embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the claimed subject matter. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the claimed subject matter.

3.

What is claimed is:

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- 2 1. A wellbore fluid comprising:
- 3 an aqueous based continuous phase;
- 4 a viscoelastic surfactant; and
- a surfactant-polymer compound soluble in an aqueous solution, the surfactantpolymer compound having a hydrophobic backbone and a plurality of hydrophilic functional groups attached to the hydrophobic backbone,
 - wherein the hydrophobic backbone is the reaction product of one or more molecules having polymerizable alkene or alkyne functional groups;
 - wherein the hydrophilic functional groups are selected from: zwitterionic surfactant functional groups, anionic surfactant functional groups, cationic surfactant functional groups, and nonionic surfactant functional groups; and,
 - wherein the combination of the viscoelastic surfactant and surfactant-polymer compound form micellar assemblies.
- 16 2. The wellbore fluid of claim 1 further comprising a water-soluble inorganic salt.
- 3. The wellbore fluid of claim 1 wherein the acid form of the surfactant-polymer compound has the structure:

$$\begin{array}{c} - \begin{bmatrix} \text{CH-CH}_2 \\ \text{CH}_2 \end{bmatrix}_{x} \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 - \begin{bmatrix} \text{CH}_2 \\ \text{CH}_2 \end{bmatrix}_{x} \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{COO}^{-1} \end{array}$$

wherein x = 2 to 300,000. 1 2 4. The wellbore fluid of claim 3 wherein x = 2 to 36. 3 5. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of 5 oligo- or poly-(α-alkenyl -ω- or α-alkynyl -ω-quaternary-ammonio-N-N-dialkyl-N-6 alkylcarboxylate) or a mixture further comprising a salt of N-alkyl-N-carboxymethyl-7 N,N-dimethylammonium chloride. 8 9 6. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of 10 oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate) or 11 12 a mixture further comprising a salt of N-hexadecyl-N-carboxymethyl-N,Ndimethylammonium chloride. 13 14 15 7. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of oligo- or poly-(α-alkenyl -ω- or α-alkynyl -ω-quaternary-ammonio-N,N-dialkyl-N-16 alkylcarboxylate). 17 18 8. The wellbore fluid of claim 1 wherein the surfactant-polymer compound is a salt of 19 oligo- or poly-(1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-methylcarboxylate). 20 21 9. A wellbore fluid comprising: 22 an aqueous fluid; 23 a viscoelastic surfactant; 24 a thickener soluble in the aqueous fluid, 25 wherein the thickener has a hydrophobic oligomeric or polymeric backbone made 26 from the reaction of alkene monomer or alkyne monomer, or mixtures thereof, and 27 wherein surfactant functional groups are attached to the hydrophobic backbone, 28 wherein the surfactant functional group is selected from: zwitterionic surfactant 29 functional groups, anionic surfactant functional groups, cationic surfactant functional 30

groups, and nonionic surfactant functional groups; and,

wherein the thickener has a molecular confirmation such that the surfactant functional groups are hydrophilic and the hydrophobic oligomeric or polymeric backbone is hydrophobic; and

wherein the combination of viscoelastic surfactant and thickener form micellar assemblies such that the wellbore fluid thickener develops viscoelastic characteristics.

7 10. The wellbore fluid of claim 9 wherein the thickener has the following structure:

$$\begin{array}{c|c} \hline CH-CH_2 \\ \hline CH_2 \\ CH_2 \\ \hline CH_2 \\ CH_2 \\ \hline CH$$

10 wherein x + y = 2 to 300,000.

11. The wellbore fluid of claim 10 wherein x + y = 2 to 36.

12. The wellbore fluid of claim 11 wherein the thickener is a salt of oligo- or poly-(α -alkene - ω - or α -alkyne-co- α -alkenyl - ω - or α -alkynyl - ω -quaternary-ammonio-N,N-dialkyl-N-alkylsulfonate).

13. The wellbore fluid of claim 11 wherein the thickener is oligo- or poly-(1-heptene-co-1-hepten-7-quaternary-ammonio-N,N-dimethyl-N-propylsulfonate).

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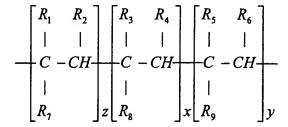
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14. The wellbore fluid of claim 9 wherein the viscoelastic surfactant is selected from the anionic, nonionic, amphoteric, zwitterionic, alcohols, alkano-lamides, following: alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, amine acetates, amine oxides, amines, sulfonated amines, sulfonated amides, betaines, block polymers, carboxylated alcohols, alkylphenol ethoxylates, carboxylic acids, fatty acids, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines, ethoxylated amides, ethoxylated fatty acids, ethoxylated fatty esters, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic surfactants, imidazolines, isethionates, lanolins, methyl esters, monoglycerides, olefin sulfonates, phosphate esters, lechithins, polyethylene glycols, polysaccharides, polyacrylic acids, polyacrylamides, propoxylated alcohols, propoxylated alkylphenols, propoxylated amines, propoxylated amides, propoxylated fatty acids, propoxylated fatty esters, protein-based surfactants, quaternary surfactants, sarcosamines, silicone-based surfactants, soaps, sodium isethionate, sorbitans, sucrose and glucose esters, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates of ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of hydrocarbons and petroleum, sulfosuccinates, taurates, and tridecyl and dodecyl benzene sulfonic acids and mixtures thereof.

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23 15. The wellbore fluid of claim 9 wherein the thickener has the following structure:



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- wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3,
- and x + y + z = 3 to 300,000 and $S_1 = CO_2^-$ or SO_3^- .

- 16. The wellbore fluid of claim 15 wherein t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1
- to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

- 17. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following
- structure:

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$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{11}
 R_{12}
 R_{12}

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wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000.

18. The wellbore fluid of claim 17 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

19. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure

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 $R_9 \text{ is}$ CH_2 N CH_2 R_{11} R_{12}

wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to 300,000, and $S_1 = CO_2$ or SO_3 .

20. The wellbore fluid of claim 19 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, x = 0 to 10, 000, y = 2 to 300,000, and z = 0 to 10,000.

21. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

$$\begin{array}{cccc}
6 & & & & \\
7 & & R_8 \text{ is} & & & & \\
& & & & \\
\end{array}$$

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$$R_9$$
 is
 CH_2
 R_{12}
 R_{12}

- wherein, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000.
- 19 22. The wellbore fluid of claim 21 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.
- 22 23. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

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$$R_9$$
 is
 CH_2
 R_{11}
 R_{12}
 R_{12}

- wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , and t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 3,
- and x + y + z = 3 to 300,000 and $S_1 = CO_2^-$ or SO_3^- .

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- 19 24. The wellbore fluid of claim 23 wherein t = 12 to 16, u = 6 to 12; v = 12 to 18, w = 1
- 20 to 3, x = 0 to 10,000, y = 2 to 300,000 and z = 0 to 10,000

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- 22 25. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following
- 23 structure:

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wherein R_1 , R_2 , R_3 , R_4 , R_5 , $R_6 = H$ or CH_3

$$R_8$$
 is $-\begin{bmatrix} CH_2 \end{bmatrix}_u$

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10 R_9 is CH_2 N R_{11} R_{12} R_{12}

wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, and x + y + z = 3 to 300,000.

19 28. The wellbore fluid of claim 25 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w 20 = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

27. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

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wherein R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, x + y + z = 3 to 300,000, and $S_1 = CO_2$ or SO_3 .

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28. The wellbore fluid of claim 27 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

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22 29. The wellbore fluid of claim 9 wherein the oligomer or polymer has the following structure:

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$$R_9$$
 is
 CH_2
 N
 CH_2
 R_{11}
 R_{12}
 R_{12}

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wherein, R_{10} , R_{11} , $R_{12} = H$ or CH_3 , t = 1 to 16, u = 6 to 12, v = 1 to 18, w = 1 to 12, and x + y + z = 3 to 300,000.

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30. The wellbore fluid of claim 29 wherein t = 12 to 16, u = 6 to 12, v = 12 to 18, w = 1 to 3, and x = 0 to 10,000, y = 2 to 300,000, and z = 0 to 10,000.

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31. The wellbore fluid of claim 9 wherein the oligomers or polymers are crosslinked with polyvalent metal ions, formaldehyde, or glutaraldehyde.

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- 32. The wellbore fluid of claim 31 wherein the polyvalent metal ions are selected from
- 25 the following: Fe²⁺, Cd²⁺, Co²⁺, Ca²⁺, Cu²⁺, UO₂²⁺, PbO²⁺, Al³⁺, Fe³⁺, Cr³⁺, Ce³⁺, Ti⁴⁺,
- 26 Zr⁴⁺, Sn⁴⁺ and mixtures thereof.

- 28 33. A method of making a wellbore fluid comprising blending:
- 29 an aqueous fluid phase;
- a viscoelastic surfactant;
- a water-soluble inorganic salt;

an oligomer or polymer soluble in an aqueous salt solution, the oligomer or polymer comprising a hydrophobic oligomeric or polymeric backbone made from the oligomerization or polymerization of alkene or alkyne monomer groups, or mixtures thereof, the oligomer or polymer further comprising zwitterionic functional groups attached to the hydrophobic backbone, wherein the oligomer or polymer is hydrophilic in the zwitterionic functional groups and hydrophobic in the backbone hydrocarbon chain to form micellar assemblies such that the oligomers or polymers develop viscoelastic character prior to a polymerization step.

34. The method of claim 33 further comprising a polymerization step of the polymer or oligomer, then drying the product and subsequently admixing it into a solution of conventional surfactants.

14 35. A method of drilling a subterranean well, the method comprising:

drilling the subterranean well using a rotary drilling rig and circulating a drilling fluid in the subterranean well, wherein the drilling fluid is the wellbore fluid of claim 1.

36. A method of reducing the loss of fluid out of a subterranean well, the method comprising injecting into the subterranean well a wellbore fluid as recited in claim 1.

ABSTRACT

Compositions for increasing the thermal and pressure stability of well fluids
viscosified using viscoelastic surfactants, the compositions including an effective amount
of an oligomeric or polymeric compound that has a thermally stable backbone structure
and at least one pendent viscoelastic surfactant functional group. Preferred compositions
for increasing the stability of well fluids viscosified using monomeric viscoelastic
surfactants include an effective amount of an oligomeric or polymeric compound that has
a thermally stable backbone structure and a multiplicity of pendent viscoelastic surfactant
functional groups attached to said backbone structure through relatively long
hydrocarbon chains, 1 to 18 carbons in length.

MAY 1 1 2006 W

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of:

Serial No.: 10/620,041

Filed: July 15, 2003

For: SURFACTANT-POLYMER COMPOSITIONS OF

ENHANCING THE STABILITY OF

VISCOELASTIC-SURFACTANT BASED FLUID

Group Art Unit: 1712

Confirmation No.: 7482

Examiner: Charles R. Richards

Atty. Dkt. No.: PA-00146US

DECLARATION OF LEAH BARDIN IN SUPPORT OF PETITION UNDER 37 C.F.R. § 1.47

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

I, Leah Bardin, hereby declare the following:

- 1. I am currently employed as the patent paralegal of M-I L.L.C. and was at the time of the following occurrences.
- 2. On or about September 21, 2005, I attempted to locate Ms. Kamlia B. Abdur-Rahman via telephone book, internet and telephone, without success.
- 3. On September 21, 2005, I sent a certified letter, return receipt requested, to Ms. Abdur-Rahman enclosing the patent application and transmittal letter, Declaration she had previously signed but not dated, and a new Declaration for her execution. Also enclosed was a FedEx return envelope for her use in returning the document to us. I received the entire package back from the post office stating "return to sender, attempted not known."
- 4. On April 21, 2006, I contacted Human Resources at M-I L.L.C. and received the last known address for Ms. Abdur-Rahman on file, for which I then sent another certified letter, return receipt requested, to her enclosing the patent application and transmittal letter, Declaration

Serial No.: 10/620,041 Confirmation No.: 7482 Applicant: Robert Horton, et al.

Atty. Ref.: PA-00146US

she had previously signed but not dated, the Assignment she signed and dated, July 1, 2003 and a new Declaration for her execution. Also enclosed was a return FedEx envelope for her use in returning the document to us. To date, I have not received the newly executed Declaration.

5. I hereby declare that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

May 11, 2006

Leah Bardin